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Title: Equation of state (EOS) for computational multi-physics

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Intended for: lecture for class given by Scott Runnels of XCP at CU Boulder

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Equation of State (EOS) for computational multi-physics

Danny Rehn
July X, 2019

What is an equation of state?



WIKIPEDIA
The Free Encyclopedia

Equation of state

In physics and thermodynamics, an **equation of state** is a thermodynamic equation relating state variables which describe the state of matter under a given set of physical conditions, such as pressure, volume, temperature (**PVT**), or internal energy.^[1] Equations of state are useful in describing the properties of fluids, mixtures of fluids, solids, and the interior of stars.

- ▶ Want to know: a material's response to different environments
- ▶ General form:
$$f(P, V, T) = 0$$
- ▶ Example: ideal gas

$$PV - nRT = 0$$

https://en.wikipedia.org/wiki/Equation_of_state

Why do we need EOS for hydro codes?

- ▶ 3 conservation equations, 4 variables ($\rho, P, \mathcal{E}, \mathbf{u}$)

$$\partial_t \rho + \nabla \cdot (\rho \mathbf{u}) = 0$$

$$\partial_t (\rho \mathbf{u}) + \nabla \cdot (\rho \mathbf{u} \mathbf{u}) + \nabla P = 0$$

$$\partial_t (\rho \mathcal{E}) + \nabla \cdot (\rho \mathcal{E} \mathbf{u}) + \nabla \cdot (P \mathbf{u}) = 0$$

- ▶ need “closure” (constitutive relations)

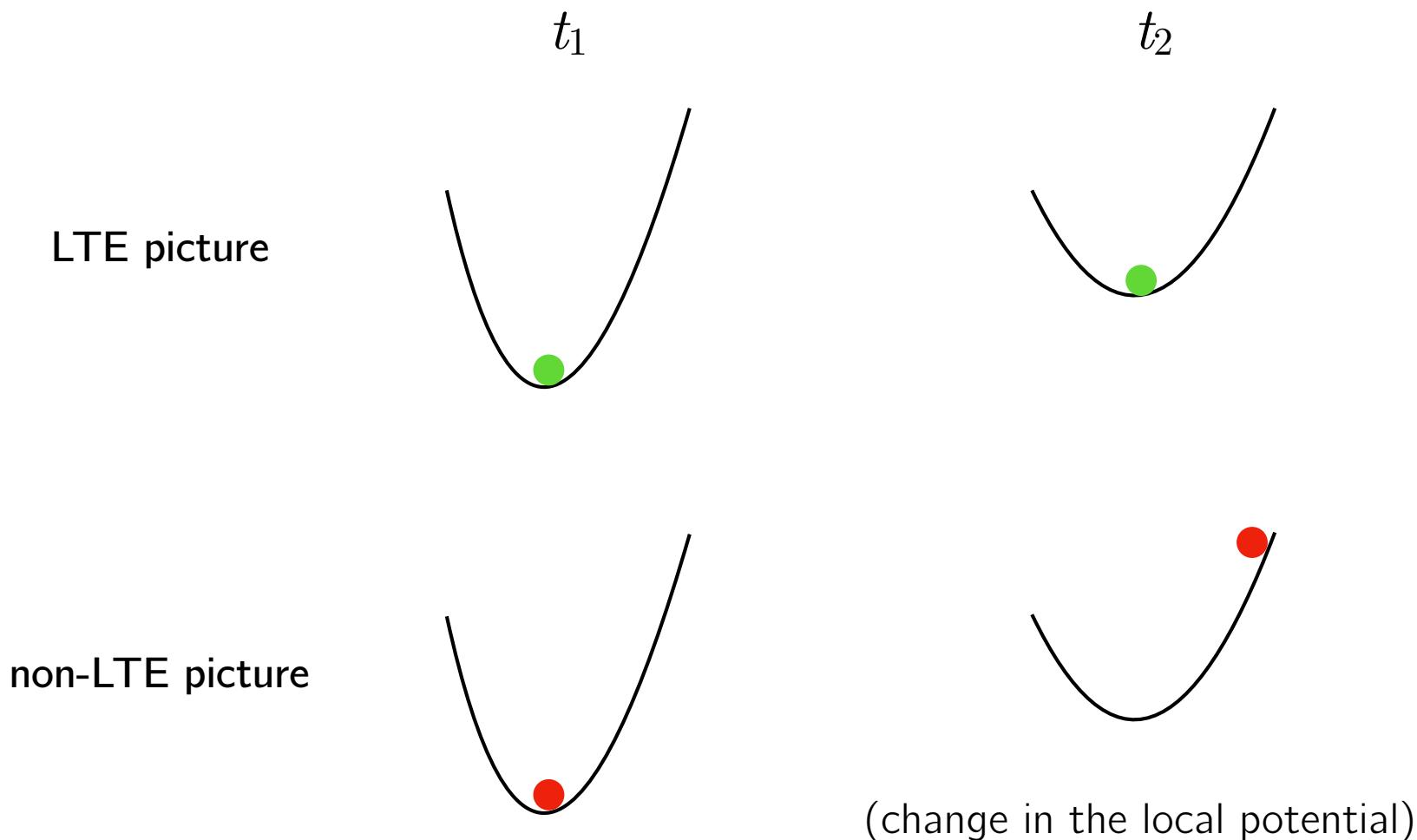
⇒ get from equation of state (EOS)

- ▶ For other multiphysics codes (magnetohydrodynamics, strength, fracture, radiation)
 - ▶ need additional conservation equations and additional closure equations

Menikoff & Plohr, *Rev. Mod. Phys.* **61**, 1 (1989).

Thermodynamic material response

- ▶ Any material response occurs as a function of time (t)
- ▶ What assumptions are we making by using thermodynamic relations in our EOS?
 - ▶ local thermal equilibrium (LTE) / adiabatic



Different thermodynamic potentials are used for different applications

hydro codes

at each timestep, update $T(V, E)$ and $P(V, E)$

where do we get T and P from?

experiments	equation of state	shock physics	phase transitions
$F(V, T)$	$F(V, T)$	$E(V, S)$ or $H(S, P)$	$F(V, T)$ or $G(T, P)$

Example: How do we get T , P from F ?

$$\left. \frac{\partial F}{\partial V} \right|_T = -P$$

$$\left. \frac{\partial F}{\partial T} \right|_V = -S$$

$$E = F + TS \quad \text{can use to get T}$$

A.E. Mattsson, *Sandia Report 2016-2112* (2016).

Brief history of EOS

PHYSICAL REVIEW

VOLUME 105, NUMBER 1

JANUARY 1, 1957

Extension of the Thomas-Fermi-Dirac Statistical Theory of the Atom to Finite Temperatures

R. D. COWAN, *Los Alamos Scientific Laboratory of the University of California, Los Alamos, New Mexico*



PHYSICAL REVIEW

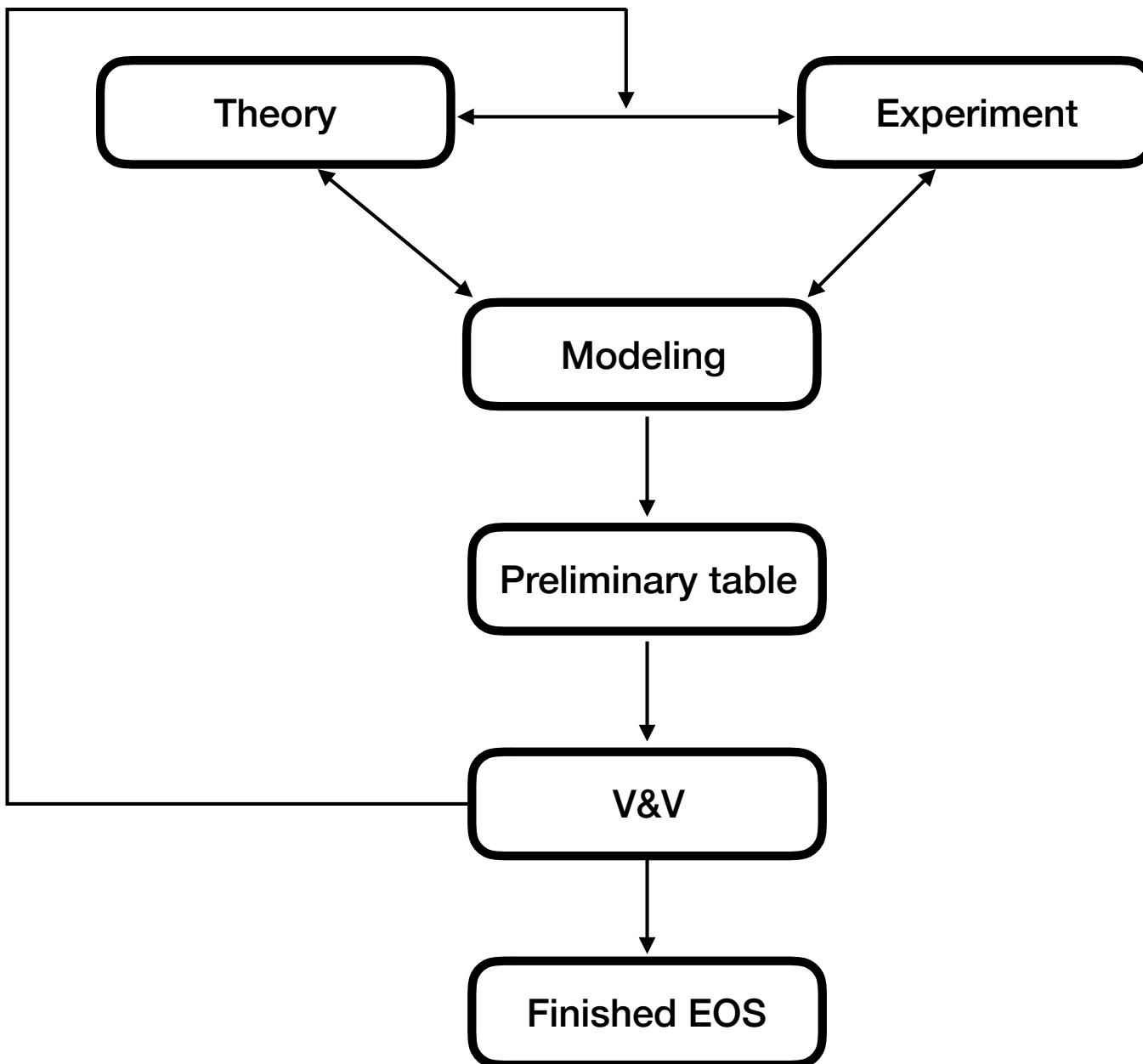
VOLUME 75, NUMBER 10

MAY 15, 19

Equations of State of Elements Based on the Generalized Fermi-Thomas Theory*

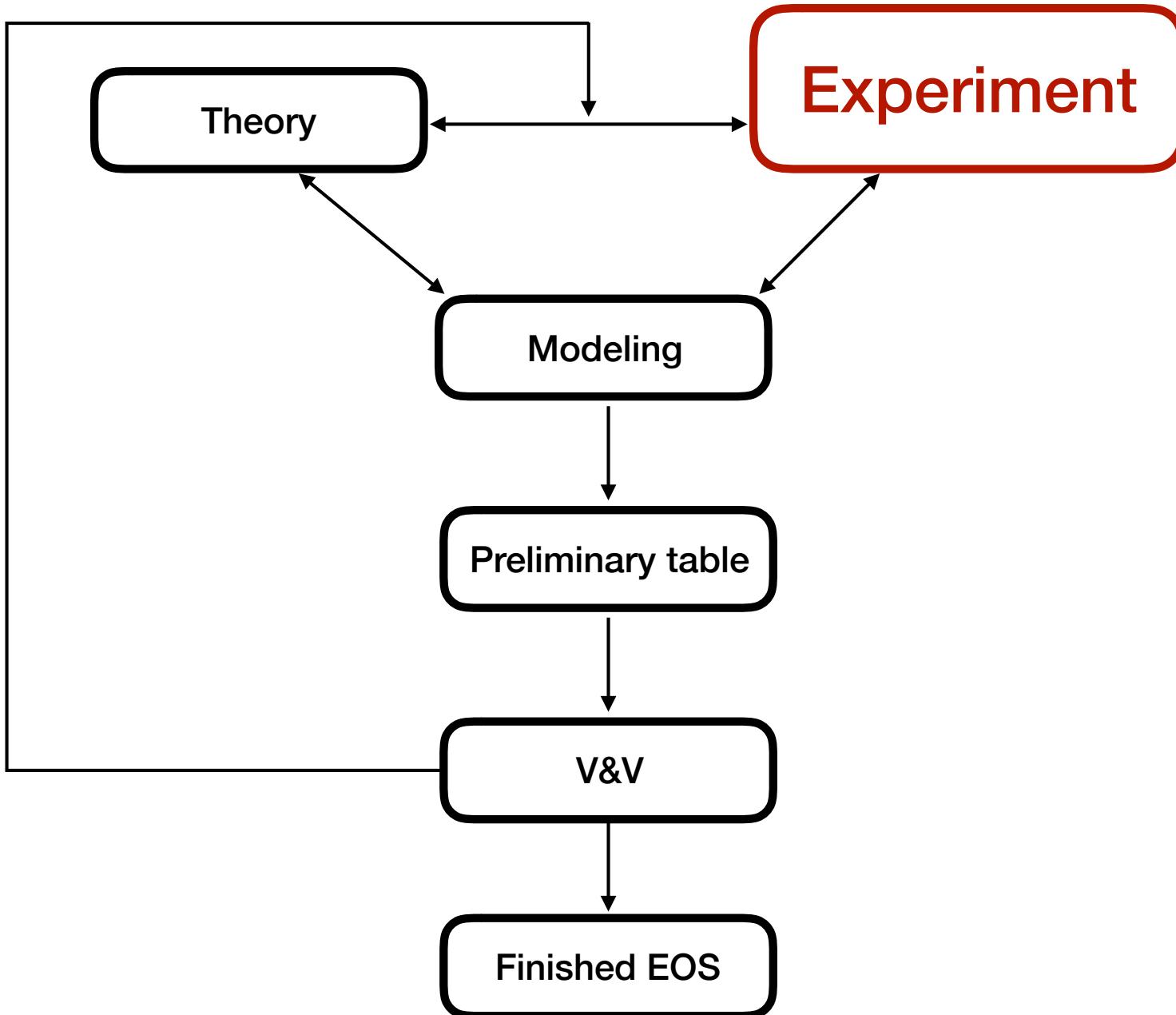
R. P. FEYNMAN, ** N. METROPOLIS, AND E. TELLER***
Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico
(Received January 21, 1949)

Overview of EOS development



S. Crockett, LA-UR 08-03680.

Overview of EOS development

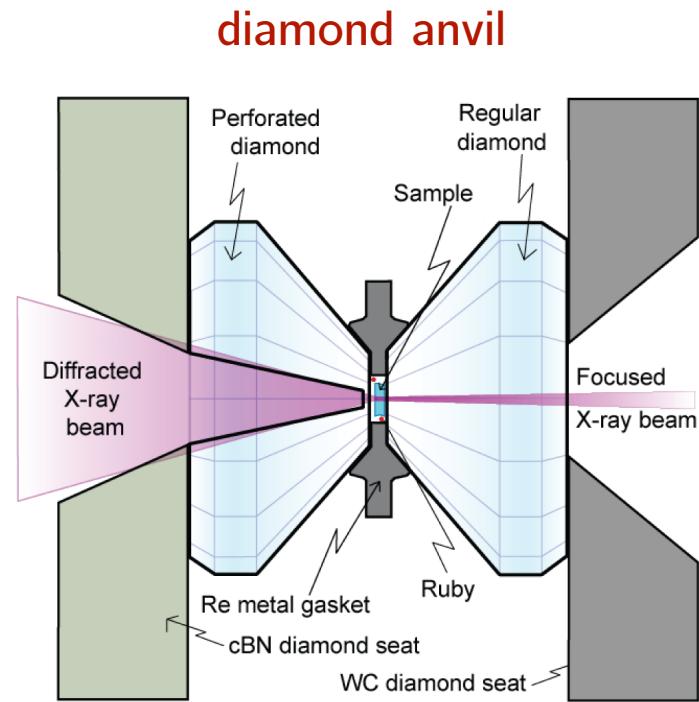


S. Crockett, LA-UR 08-03680.

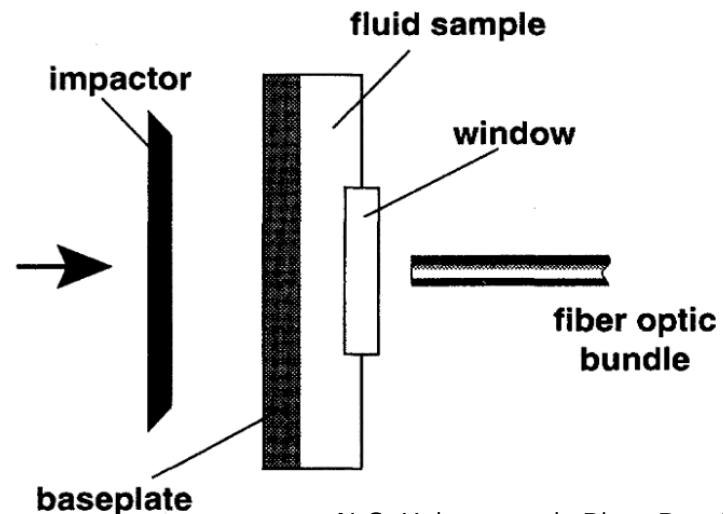
Experimental input

- ▶ Ambient pressures:
 - ▶ density
 - ▶ melting/boiling point
 - ▶ thermal expansion
 - ▶ elastic moduli, phonon data
 - ▶ specific heat

- ▶ High pressures:
 - ▶ melt curves
 - ▶ shock (Hugoniot) data
 - ▶ diamond anvil



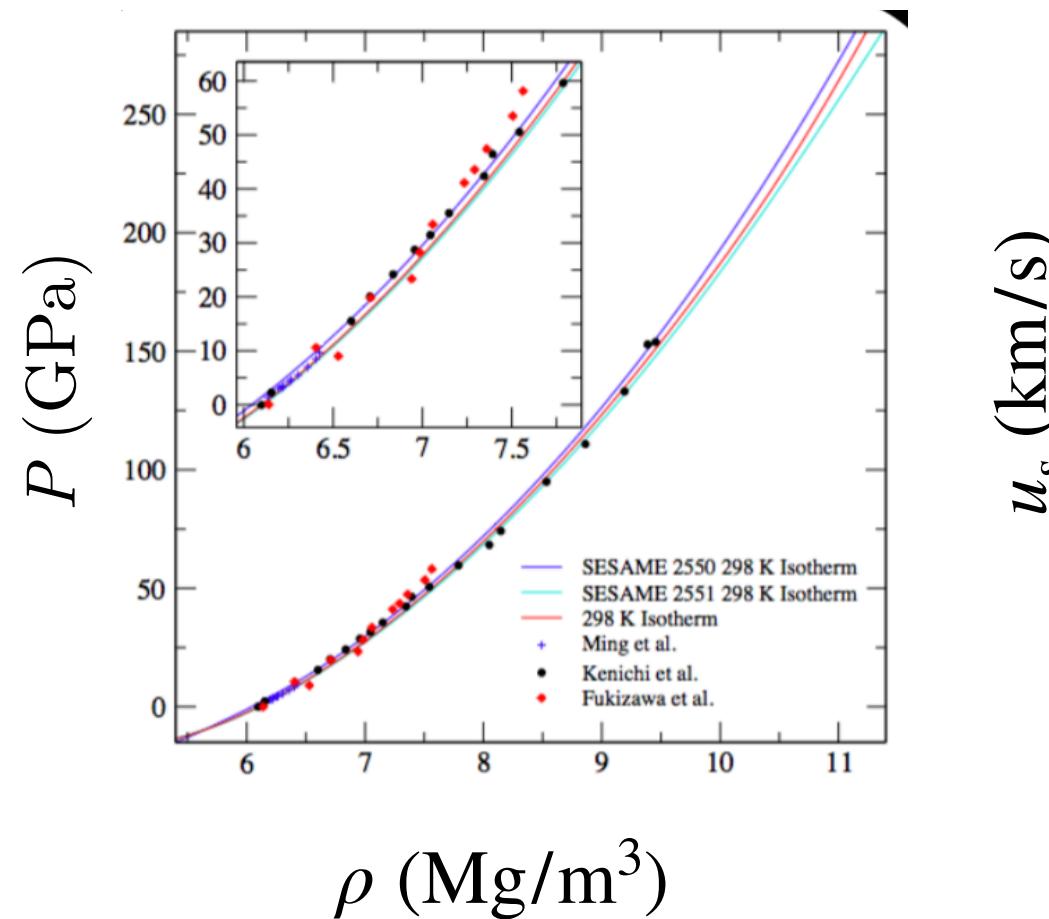
schock experiment (hugoniot)



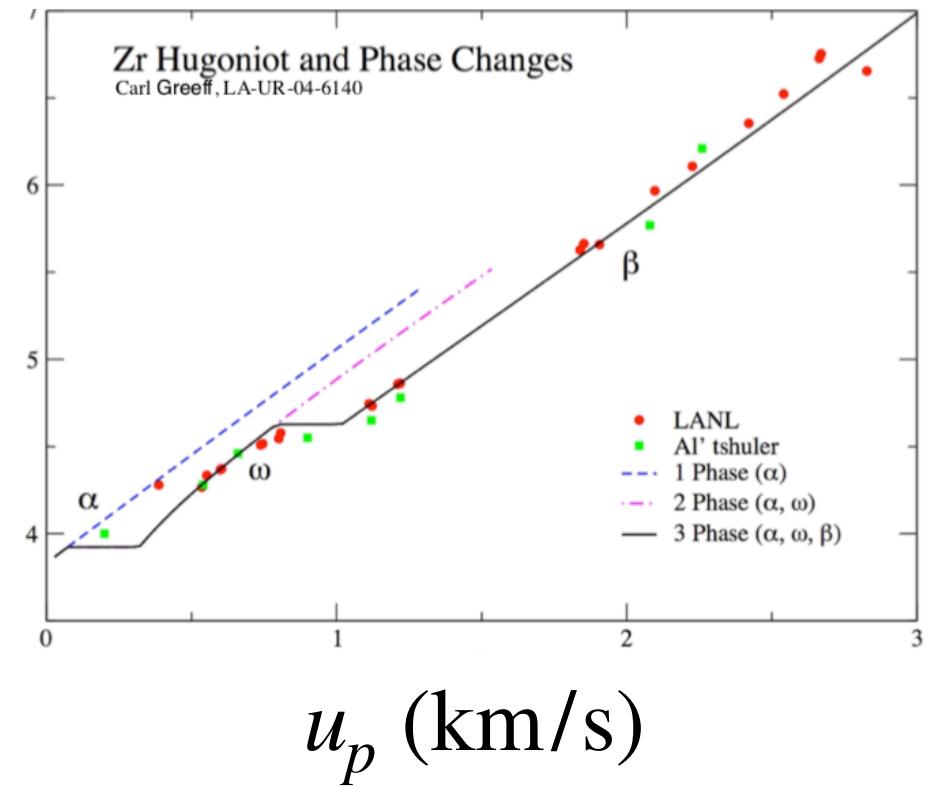
N.C. Holmes, et al. *Phys. Rev. B* **52**, 22 (1995).

Experimental input

vanadium diamond anvil

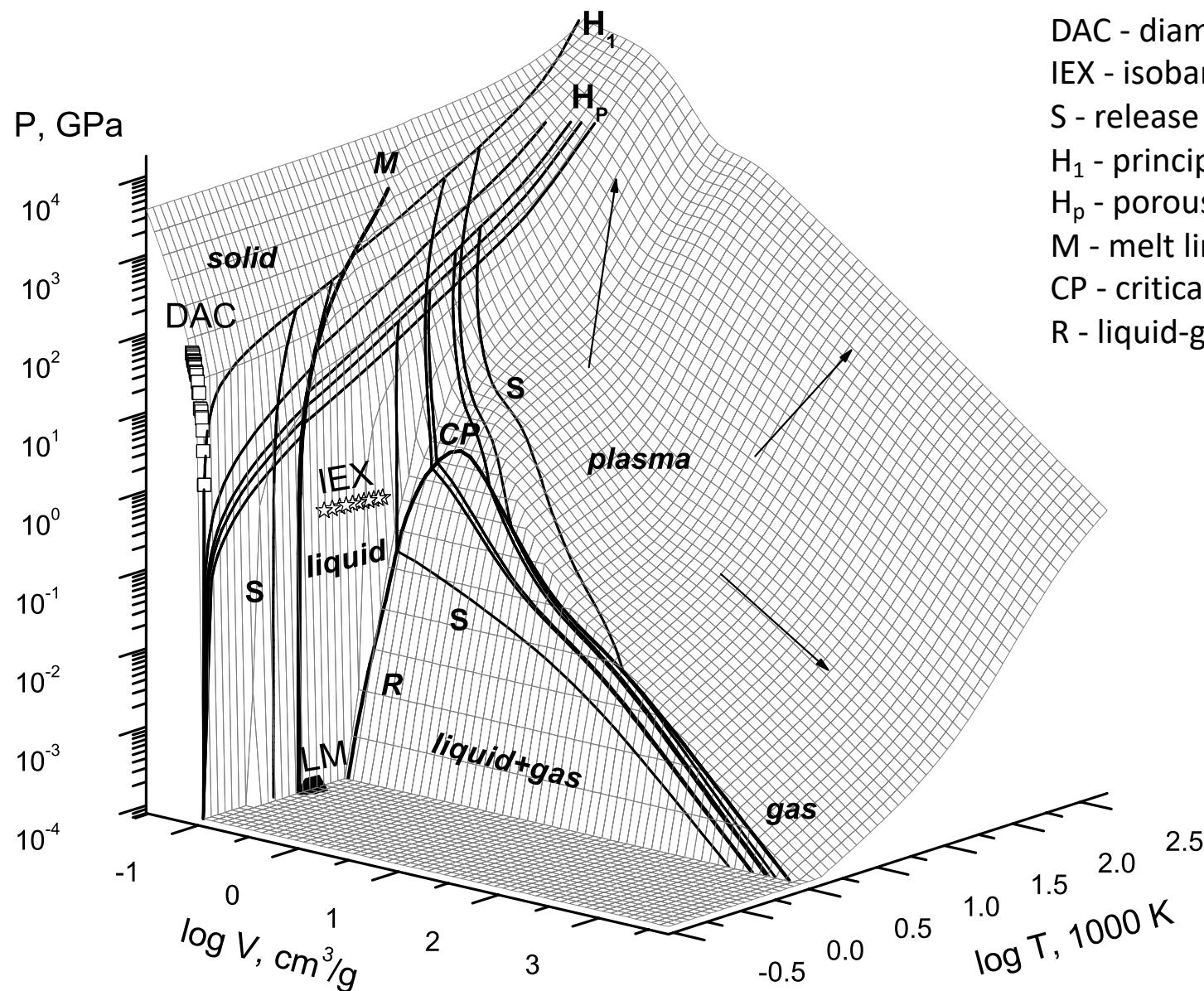


zirconium shock experiment



S. Crockett, LA-UR 08-03680.

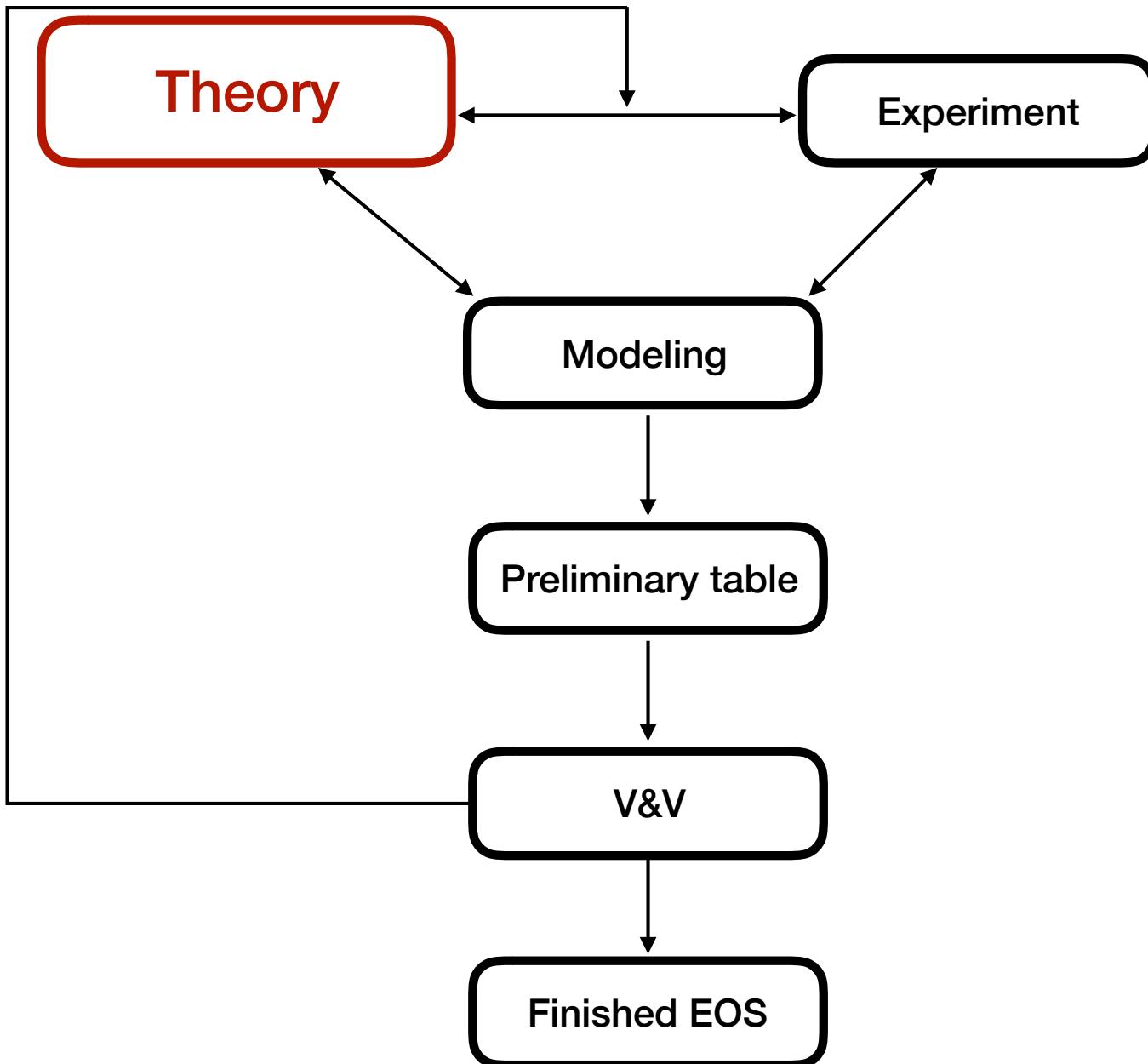
Experiments are often limited in determining the full phase diagram



DAC - diamond anvil cell measurements
IEX - isobaric expansion experiments
S - release isentropes
 H_1 - principal hugoniot
 H_p - porous hugoniotics
M - melt line
CP - critical point
R - liquid-gas boundary

Acknowledgement: J. Carpenter, Sandia. ref: SAND2012-8899C

Overview of EOS development





Very fast review of basic solid state physics I

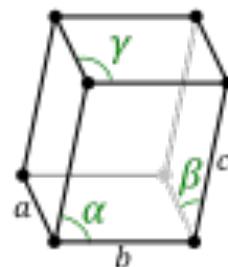
Ideal, infinite solids are **periodic**:

translation by a given set of vectors leads you to a new location with identical surroundings

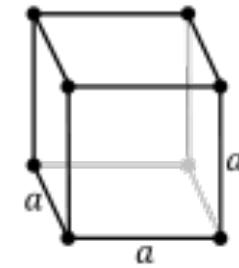
There are 14 possible "Bravais lattices" that can be used to define all periodic solids

Examples:

triclinic



cubic



When simulating solids on the computer, we use these (or larger) cells and apply **periodic boundary conditions** to determine the properties of the solid as a whole



Very fast review of basic solid state physics II

The $T = 0$ electronic properties are formally determined by solving the Schrödinger equation

$$\hat{H}\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = E\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$$

$$\hat{H} = \sum_i -\frac{\nabla_i^2}{2} + \sum_{i,I} V_I(|\mathbf{r}_i - \mathbf{R}_I|) + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + E_{II}$$

electron KE ion-electron PE electron-electron PE ion-ion PE

For large enough N (# electrons), this is impossible to solve

Basic theory for materials

Introduction to density functional theory

Question:

Rather than trying to solve for Ψ , can we use the electron density $n(\mathbf{r})$ alone?

Hohenberg and Kohn (1964): proof that $E_0 = E_0[n]$

⇒ if we know the correct functional, we can use only the density to determine the ground state properties

Basic theory for materials

Introduction to density functional theory

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⇒ if we know the correct functional, we can use only the density to determine the ground state properties

So what is the catch?

The exact functional is not known!

⇒ the past 30 years have focused on improving functionals for DFT!

R.M. Martin, *Electronic Structure*, Cambridge (2008).

Basics of Kohn-Sham DFT

Rather than using the $n(\mathbf{r})$ directly (which has limitations), set up a system of non-interacting wave functions that each satisfy

$$H[n]\psi_n(\mathbf{r}) = \varepsilon_n \psi_n(\mathbf{r})$$

$$H[n] = -\frac{\nabla^2}{2} + \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{\text{xc}}[n](\mathbf{r})$$

$$n(\mathbf{r}) = \sum_n |\psi_n(\mathbf{r})|^2$$

electron KE

electron-electron

exchange, correlation

This term basically is a ‘catch-all’ term that includes the effects not captured in the first two terms

⇒ most of the ‘empiricism’ in DFT comes from this term!

R.M. Martin, *Electronic Structure*, Cambridge (2008).

Choosing an exchange-correlation functional in DFT

► LDA vs. GGA vs. meta-GGA

There are a few different ‘classes’ of exchange-correlation functionals out there

LDA (local density approx.)

expression for xc uses only $n(\mathbf{r})$

GGA (generalized gradient approx.)

expression for xc uses $n(\mathbf{r})$ and $\nabla n(\mathbf{r})$

meta-GGA

expression for xc uses $n(\mathbf{r})$, $\nabla n(\mathbf{r})$, and $\nabla^2 n(\mathbf{r})$

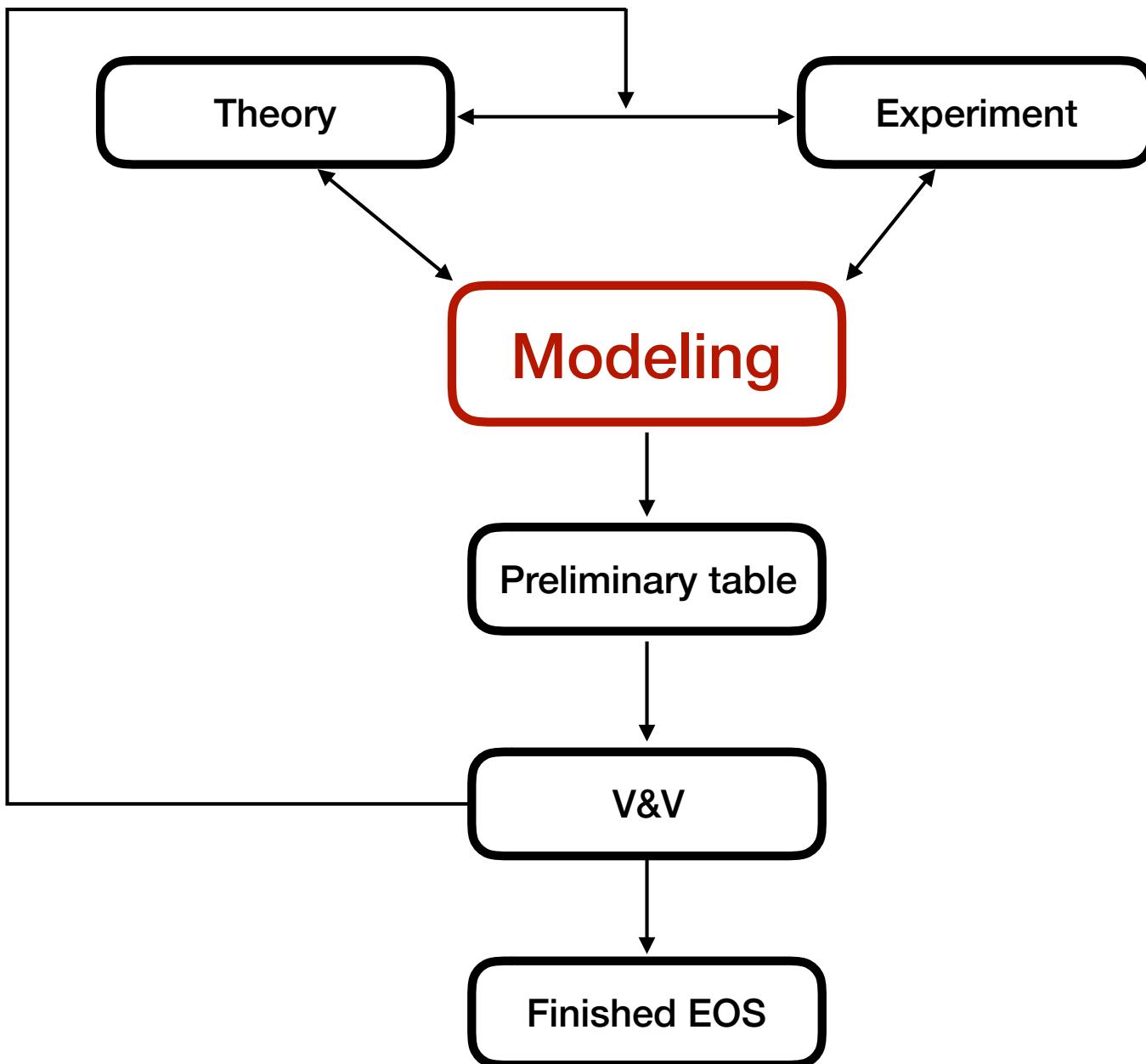
Note: more gradients does not necessarily mean better results!!

3 take-away messages about DFT

1. DFT is in principle exact, but for practical reasons is still approximate!
2. DFT cannot do everything, but it is usually qualitatively correct for ground-state properties and gives surprisingly accurate quantitative predictions
3. The main approximation made in DFT is the exchange-correlation functional. Always remember that you can get different results using, e.g., LDA vs. GGA!

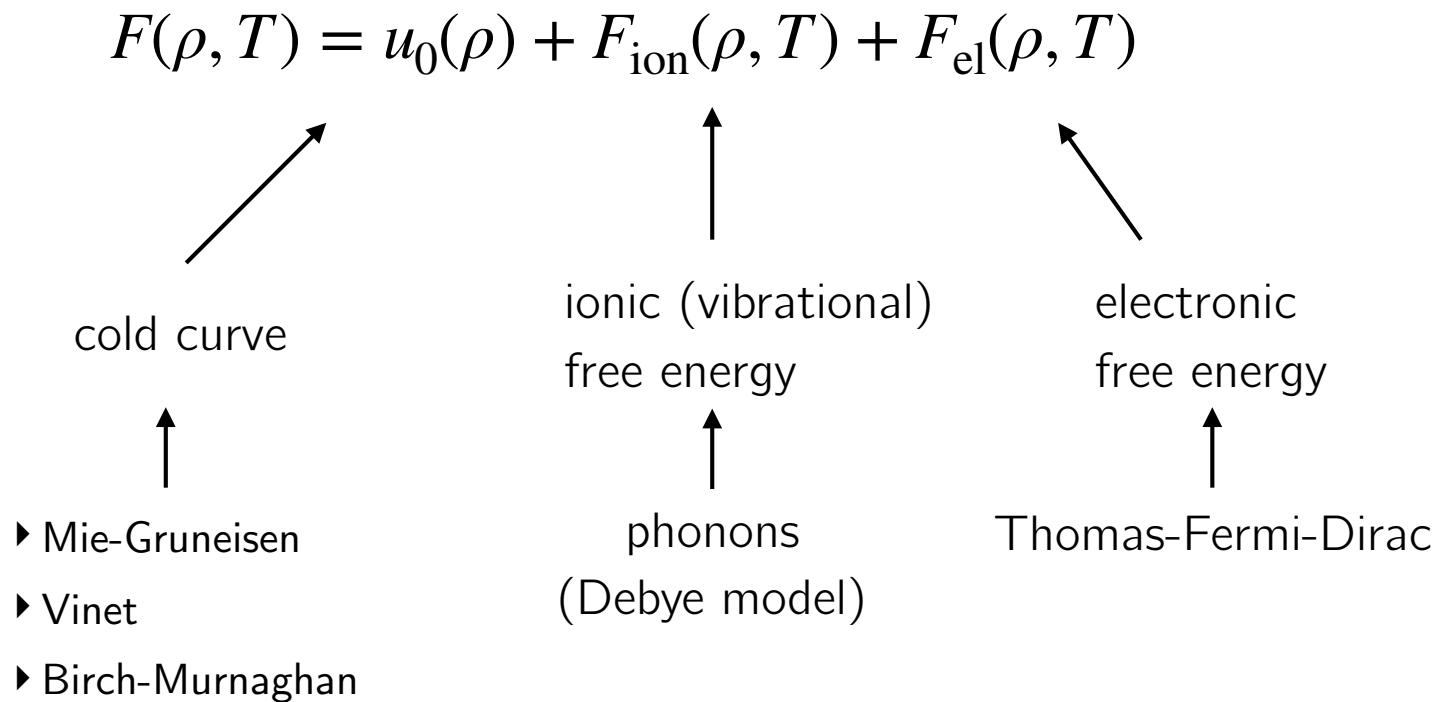
Despite these things, DFT is still extremely useful and probably the best tool we have

Overview of EOS development



Overview: how do we use ground-state DFT calculations for EOS?

The free energy is usually split into 3 terms



Cold curves: different curves are used in different circumstances

Mie-Grüeisen

$$P(\rho, T) = P_{\text{ref}}(\rho) + c(T - T_{\text{ref}})$$

computed from a Hugoniot

Vinet

$$P(\rho, T) = P_{\text{ref}}(\rho) + c(T - T_{\text{ref}})$$

computed from an isotherm

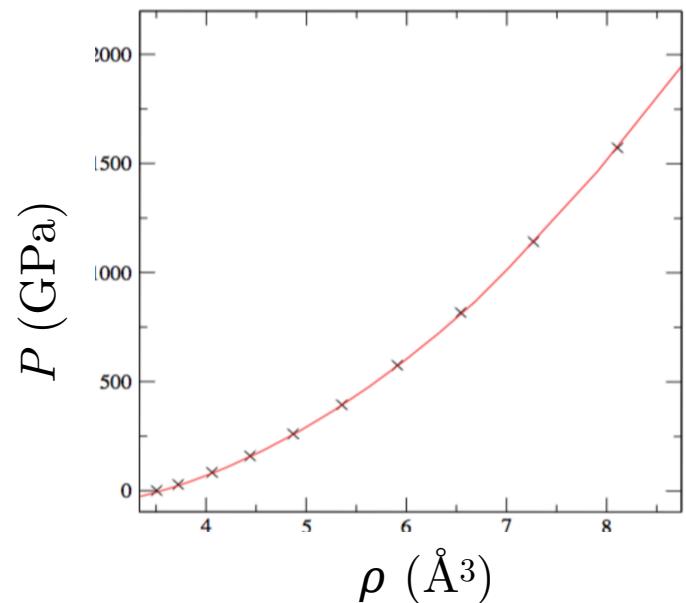
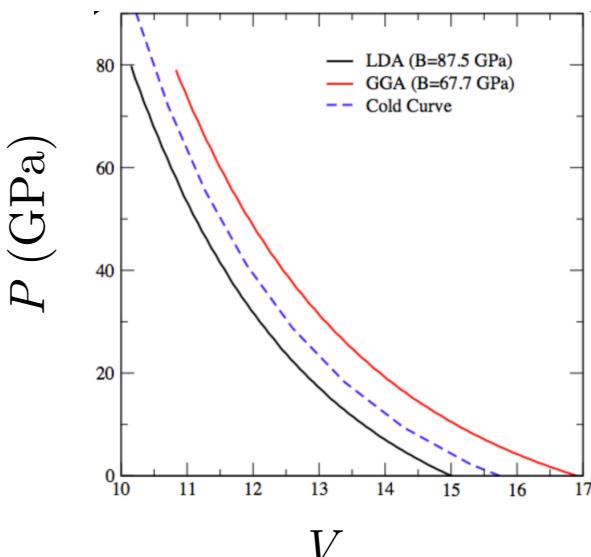
Birch-Murnaghan

$$P(\rho, T) = P_{\text{ref}}(\rho) + c(T - T_{\text{ref}})$$

computed from an isentrope

many others, as well

LiF cold curve

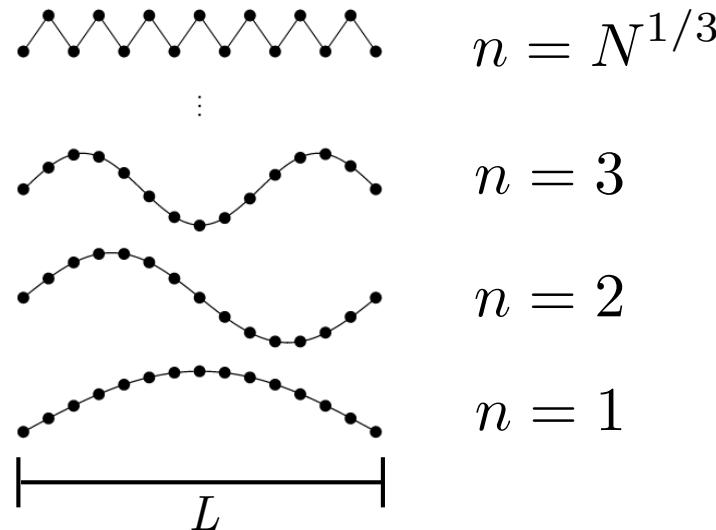
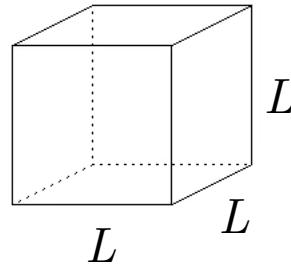


S. Crockett, LA-UR 08-03680.

$F_{\text{ion}}(\rho, T)$ for EOS usually uses comes from the Debye model

► **Debye model** (1912):

box of phonons (vibrational modes) with N atoms



$$n = N^{1/3}$$

$$n = 3$$

$$n = 2$$

$$n = 1$$



1. energy in each mode

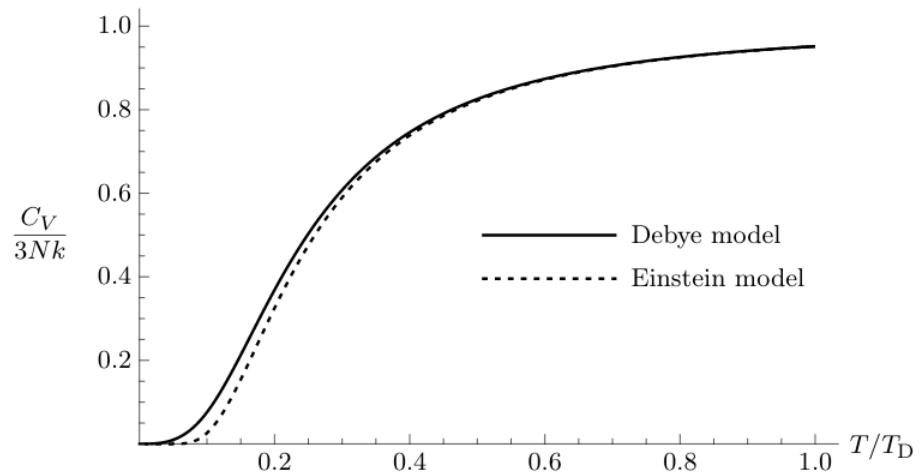
$$E_n = h\nu_n = \frac{hv_s}{\lambda_n}$$

2. total energy

$$U = 3 \int_0^{E_{\max}} \frac{E}{\exp(E/k_B T) - 1} dE$$

3. heat capacity

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

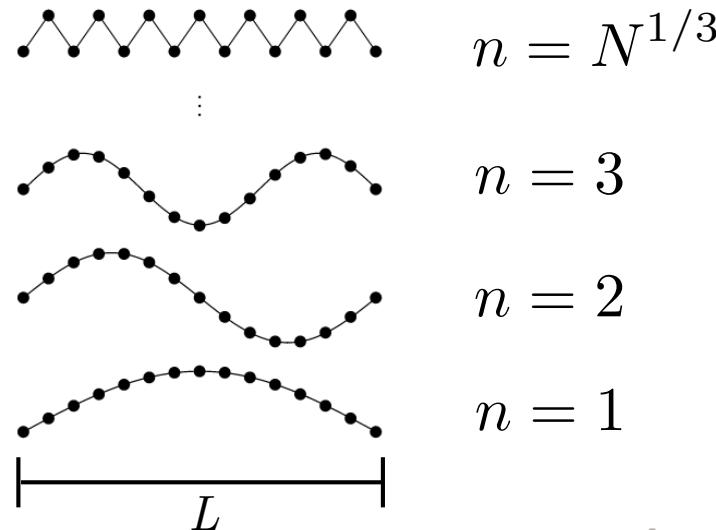
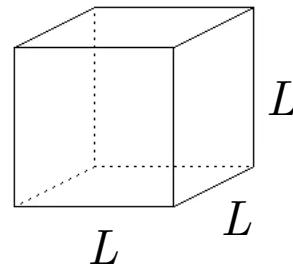


D. Schroeder, *An Introduction to Thermal Physics*, Pearson (1999).

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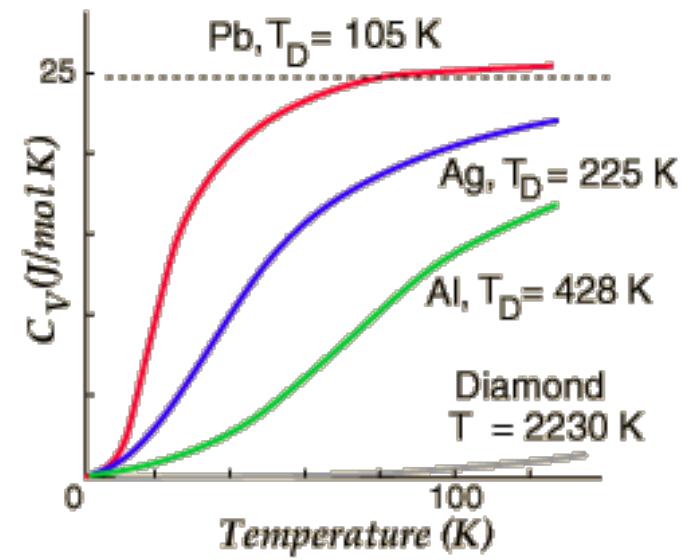
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$$C_V = \left(\frac{\partial U}{\partial T} \right)_V$$



D. Schroeder, *An Introduction to Thermal Physics*, Pearson (1999).

$F_{\text{ion}}(\rho, T)$: what is right/wrong about the Debye model?

- What is right:

low temperature behavior

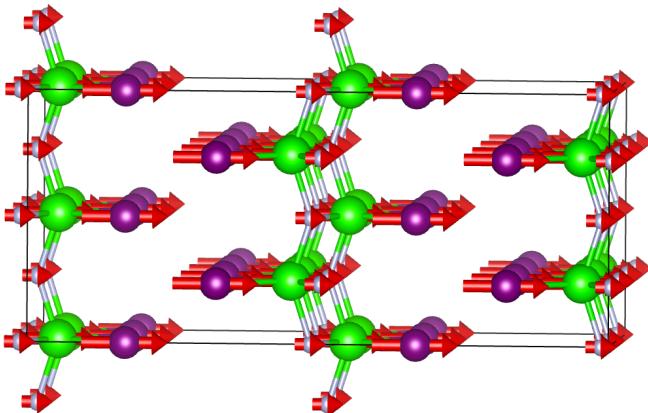
high temperature behavior

- What is wrong:

intermediate temperatures

- What would be more accurate?

calculate heat capacity, free energy, etc. directly from DFT calculations!



vibrational mode for ZrIN,
computed using DFT

Each cell has $3N$ modes

⇒ more accurately compute $F(\rho, T)$, $C_V(\rho, T)$, etc.

this level of approximation is not yet in EOS tables!

$F_{\text{el}}(\rho, T)$ for EOS usually comes from Thomas-Fermi-Dirac model

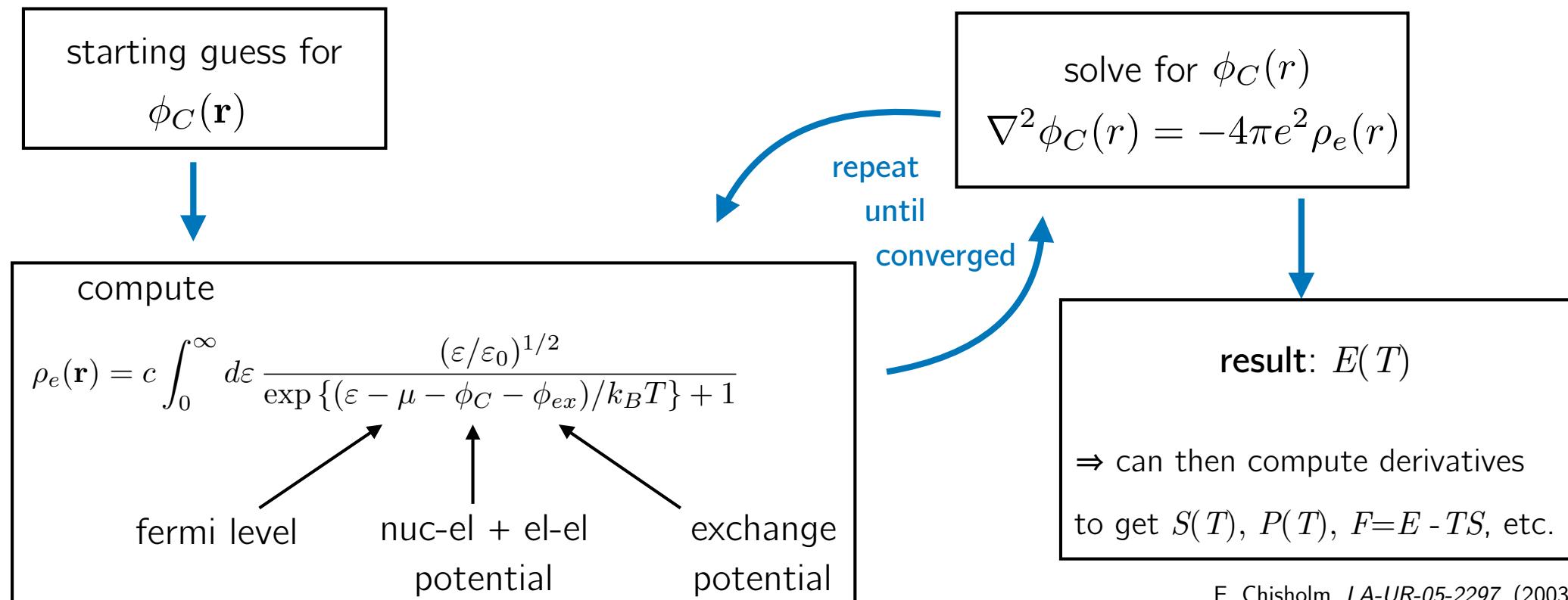
► **Thomas-Fermi model (1927)**

- semi-classical model of electrons in a material based on $\rho_e(\mathbf{r})$ and KE, PE of nuclei

► **Thomas-Fermi-Dirac model (1928)**

- extension of TF model by Dirac to incorporate an exchange contribution to the energy

How does it work?

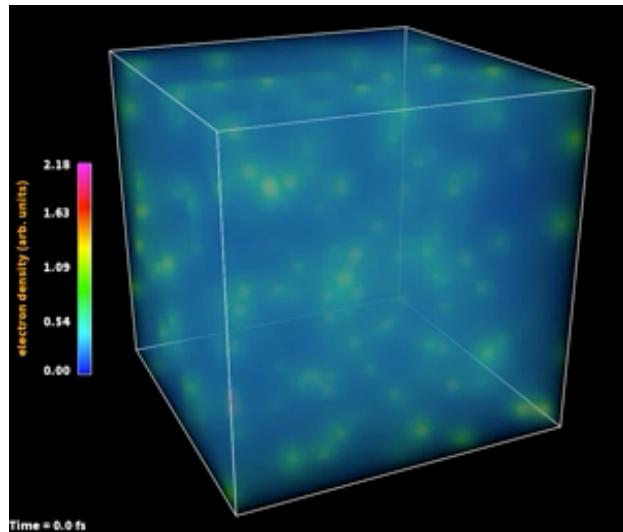


E. Chisholm, LA-UR-05-2297, (2003).

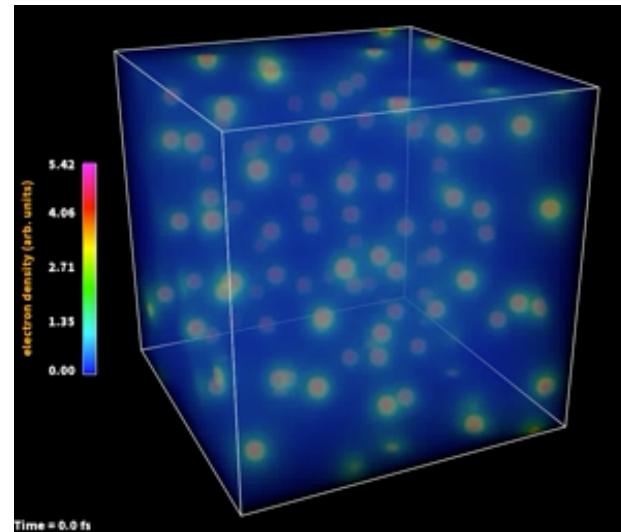
DFT-based molecular dynamics

- ▶ computationally demanding!
- ▶ can think of as 'computer experiments' at whatever P , T you want

In principle, you can get all 3 terms: $F(\rho, T) = u_0(\rho) + F_{\text{ion}}(\rho, T) + F_{\text{el}}(\rho, T)$



deuterium, 10 g/cc @ 10 eV



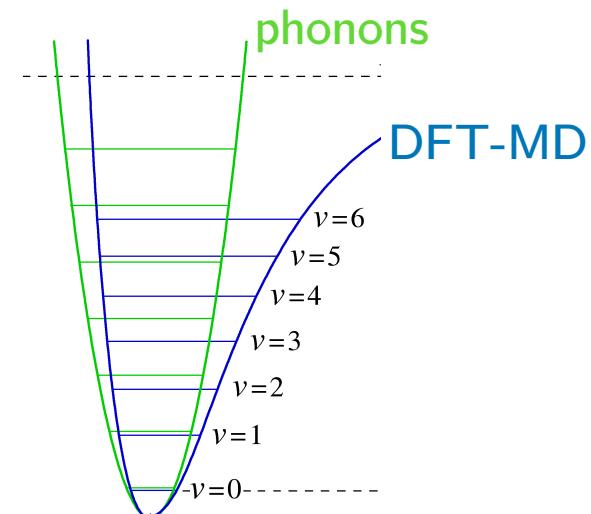
carbon, 5.7 g/cc @ 8.6 eV

video from: <https://www.lanl.gov/projects/dense-plasma-theory/research/density-functional-theory.php>

DFT-based molecular dynamics

► advantages of DFT-MD

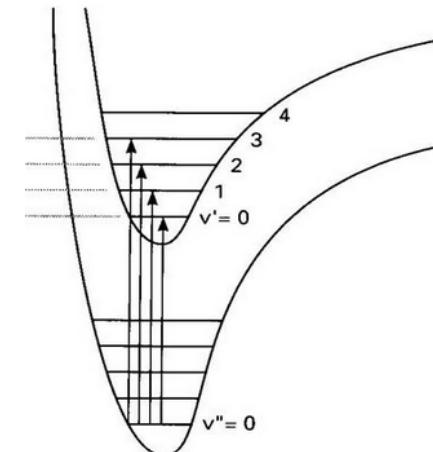
- relatively straight-forward to use
(create a cell, set temperature, let it run)
- vibrational part of the energy is more accurate than phonons
(includes anharmonic effects)



► what about electronic excitations?

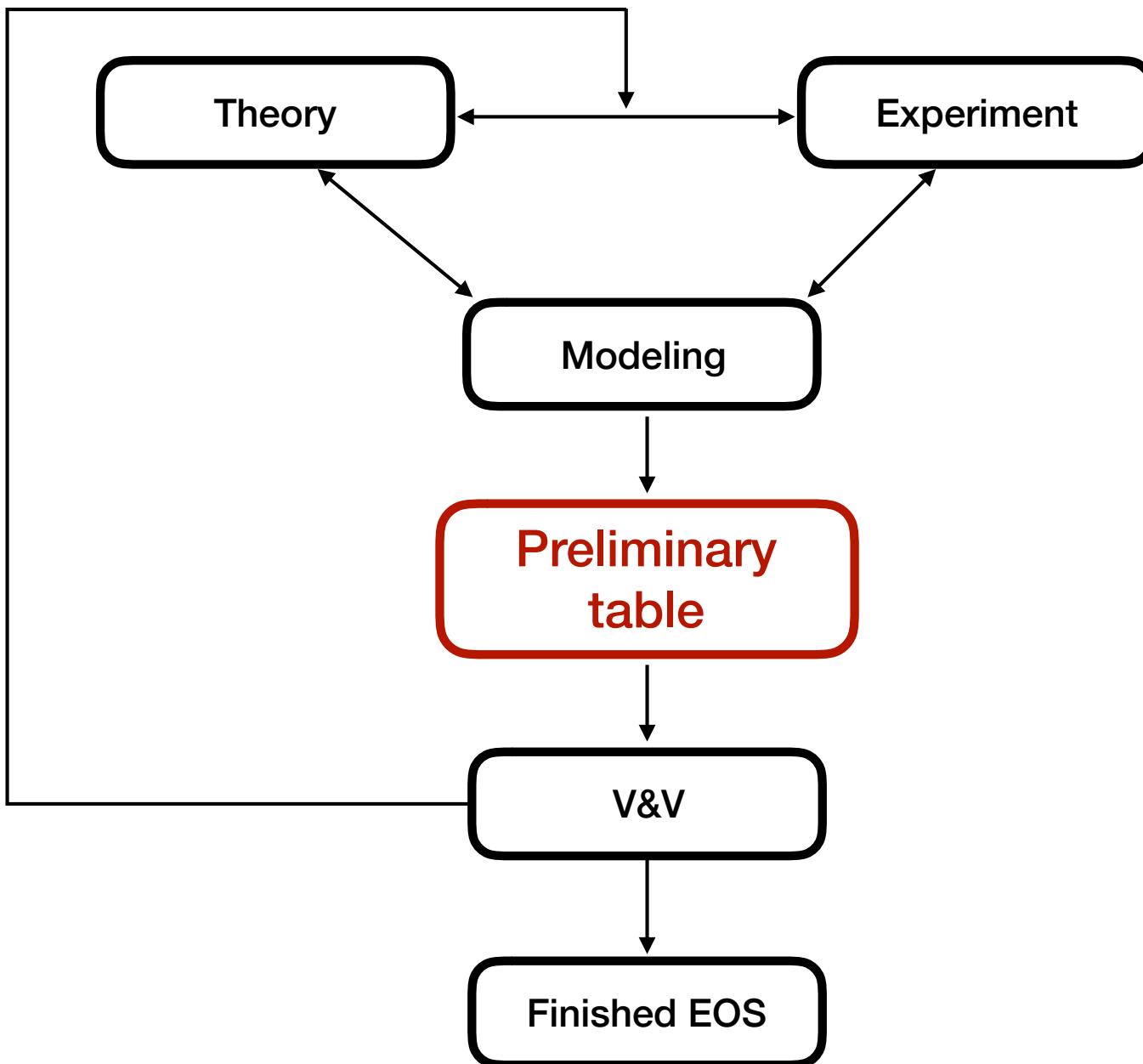
- not captured by standard DFT-MD methods
- can be very important for shocks, radiation, nuclear decay, other phenomena
- to capture, need TDDFT or 'excited state MD'

not describing this!



$$\left(-\frac{1}{2} \nabla^2 + v_s(\mathbf{r}, t) \right) \phi_i(\mathbf{r}, t) = i \frac{\partial}{\partial t} \phi_i(\mathbf{r}, t)$$

Overview of EOS development



How do we generate EOS tables?

SESAME input file for silver (Ag)

```
&job
  job _type='neweos'
/
&neweos
  material_number=2721
  material_name='silver'
  author=''
  references=''

  atomic_number=47
  atomic_weight=107.868
  reference_density=10.49

  cold_model='pressure_table'
  density_pressure_n_pairs=<# pairs in list>
  cold_densities=<list density values>
  cold_pressures=<list pressure values in GPa>

  lennard_jones_exponent=1.0
  cohesive_energy_kc=284
  upper_compression_cutoff=1.46
/
```

Basic material information

Basic atomic information

input data for cold curve

low-density regime parameters

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```
&job
  job _type='neweos'
/
&neweos
  material_number=2721
  material_name='silver'
  author=''
  references=''

  atomic_number=47
  atomic_weight=107.868
  reference_density=1.0
  cold_model='pressure_table'
  density_pressure_n_pairs=<# pairs in list>
  cold_densities=<list density values>
  cold_pressures=<list pressure values in GPa>

  lennard_jones_exponent=1.0
  cohesive_energy_kc=284
  upper_compression_cutoff=1.46
/
```

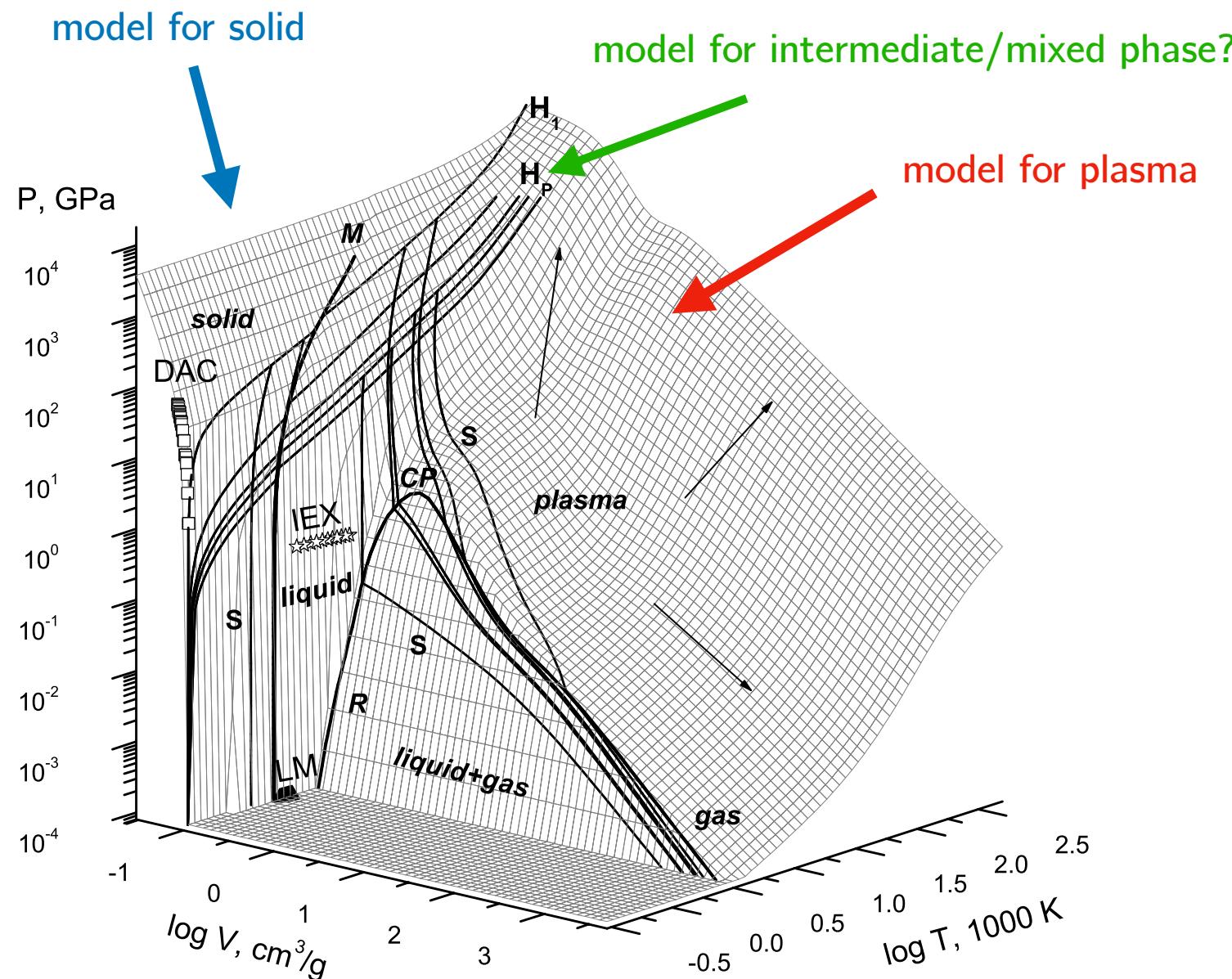
This is fitting
between high density (solid)
and low density (LJ gas)

Low density match using

$$E_c(\rho) = f_1 \rho^{f_2} - f_3 \rho^{f_{LJ}} + E_B$$
$$P_c(\rho) = \rho(f_1 f_2 \rho^{f_2} - f_3 f_{LP} \rho^{f_{LJ}})$$

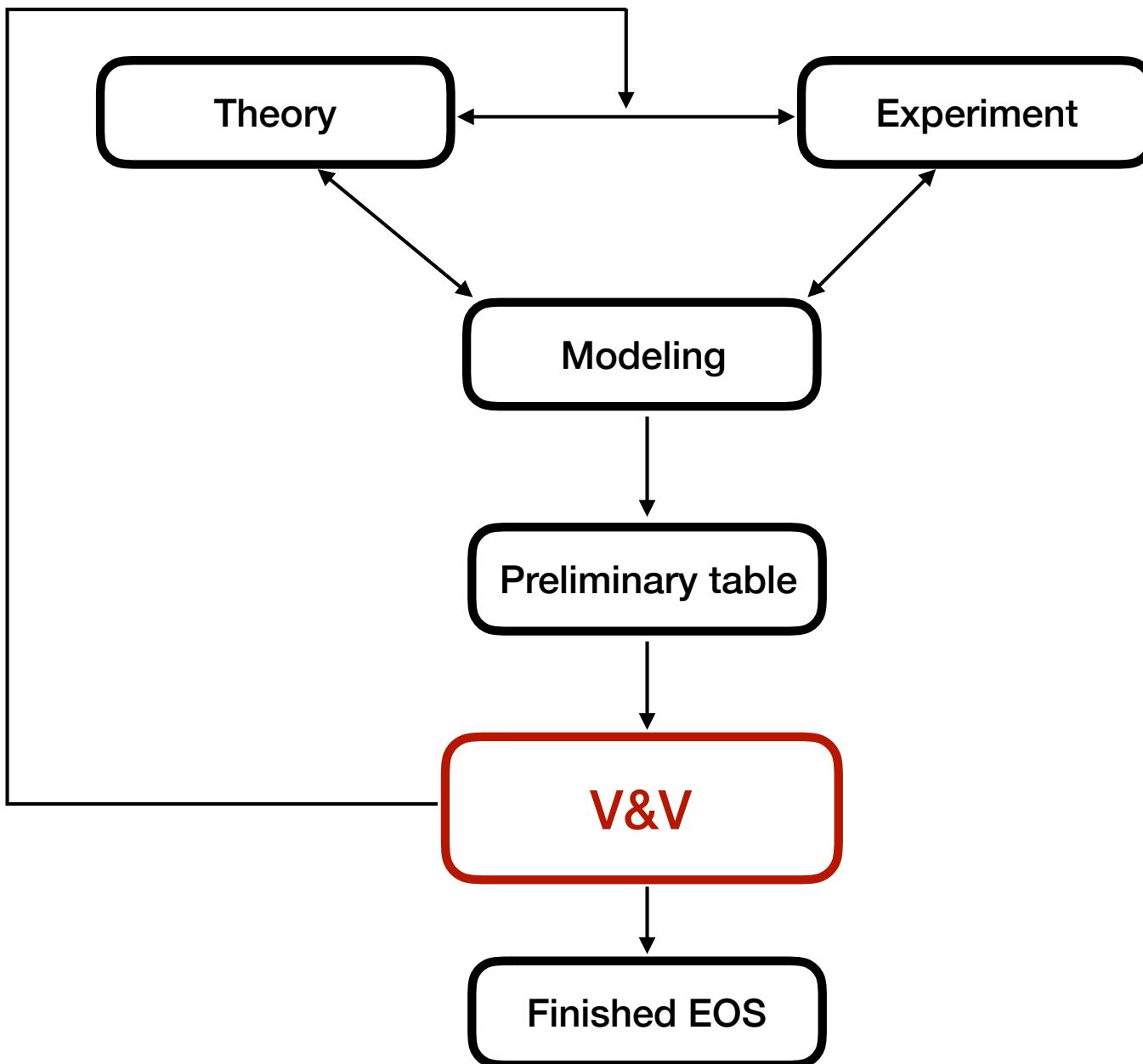
low-density regime parameters

For complicated phase diagrams, interpolating between phases becomes difficult



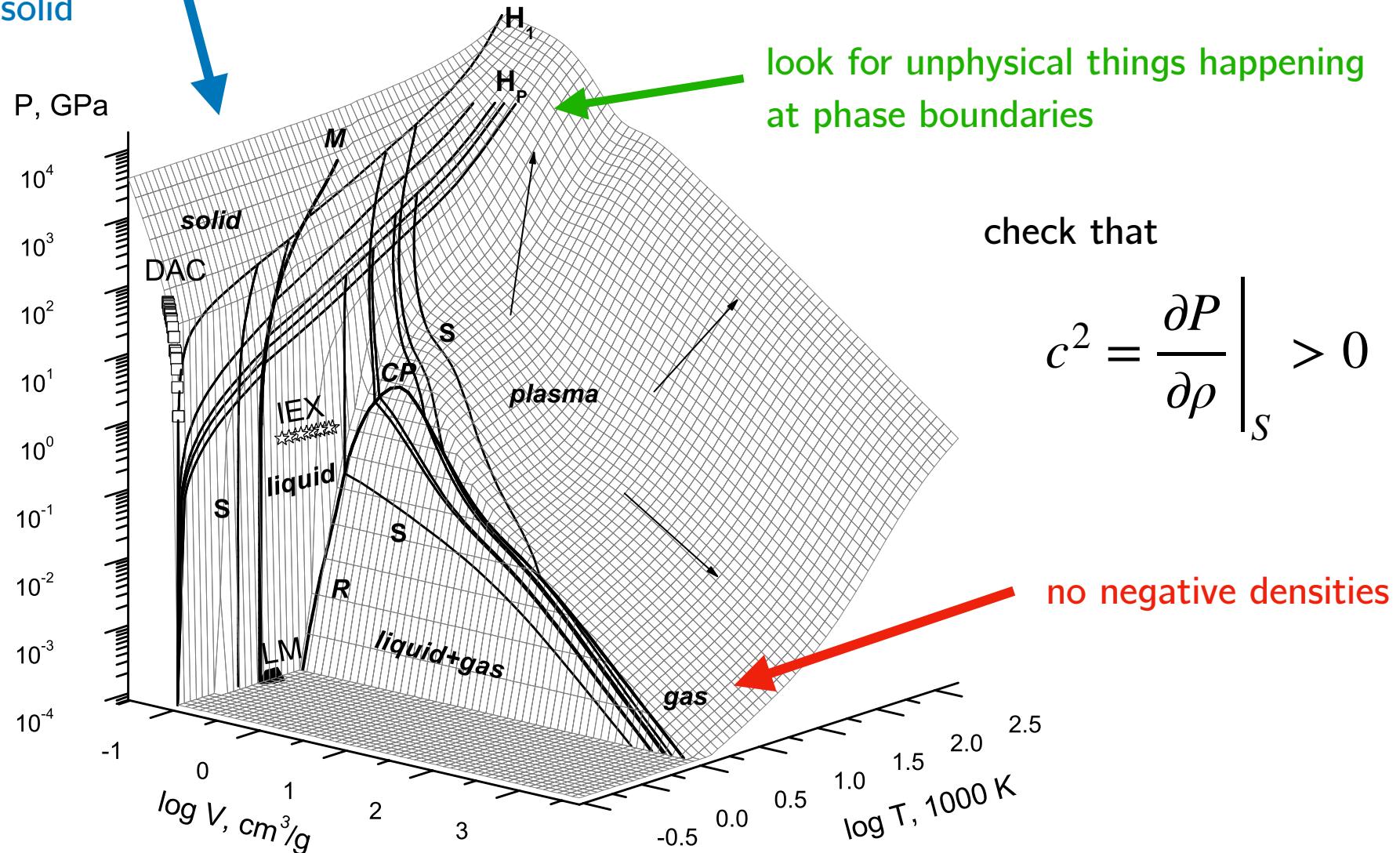
Acknowledgement: J. Carpenter, Sandia. ref: SAND2012-8899C

Overview of EOS development



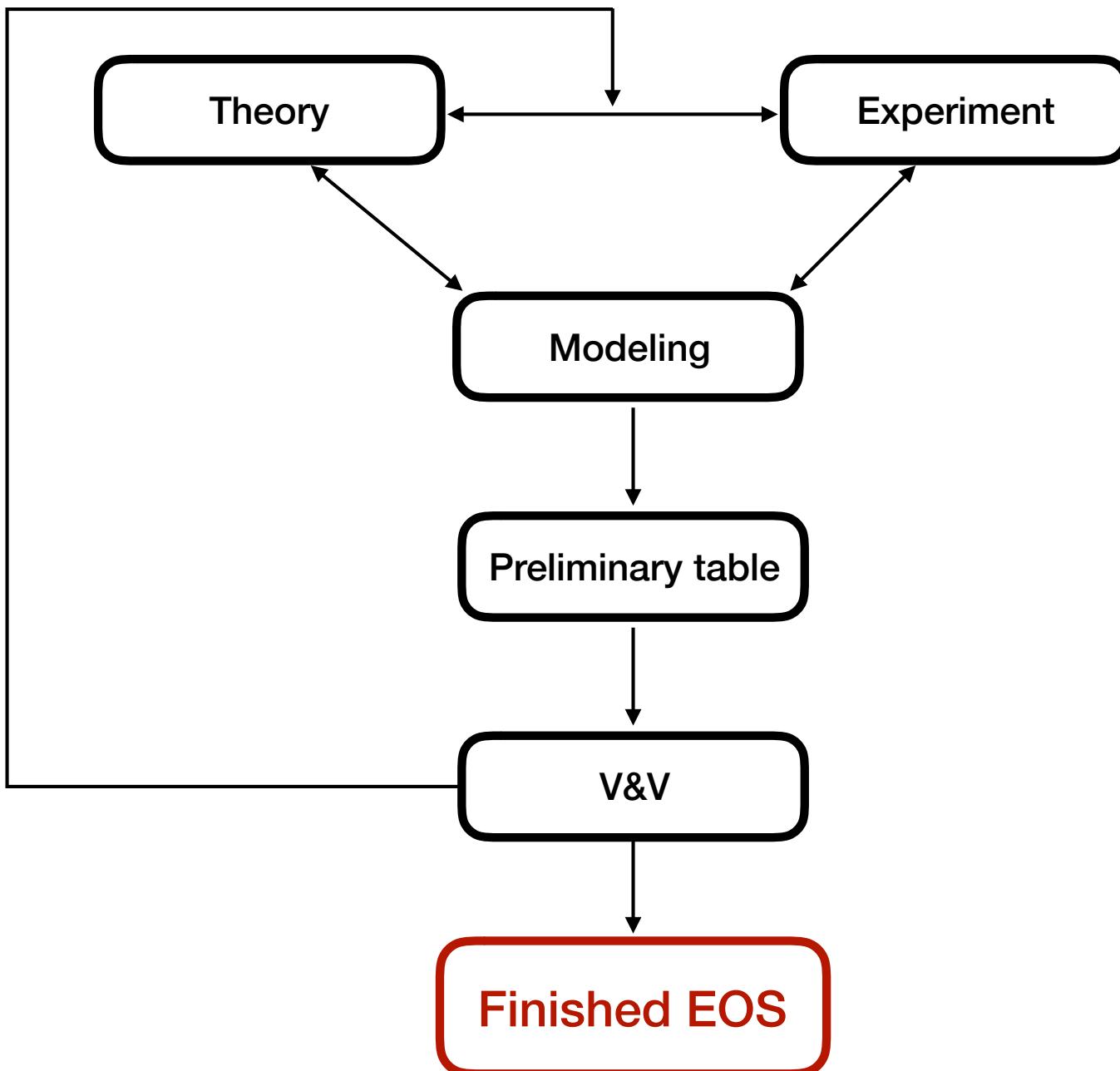
Verification and validation is important to ensure unphysical things don't happen throughout the table!

make sure the density isn't too low
to be a solid



Acknowledgement: J. Carpenter, Sandia. ref: SAND2012-8899C

Overview of EOS development



S. Crockett, LA-UR 08-03680.

Online examples of SESAME tables

There are usually multiple SESAME tables for a given material

File: MARKING	Sesame Number : Material Name	Density (gm/cc)	Source	Tables	Dates [1]
(1)sesame: UNCLASSIFIED	32720: silver (z= 47.00 a=107.87)	1.050E+01	w. slattery	101 201 411 412	09/05/90, 06/14/91
(2)sesame: UNCLASSIFIED	2721: silver (z= 47.000000 a=107.868000)	1.049E+01	Scott D. Crockett	101 102 201 301 303 304 305 306 311 401 411 412	05/10/11, 05/10/11
(3)sesou: UNCLASSIFIED	12720: silver (z=47, a=107.68)	1.049E+01	lasl t-4	101 102 201 502	09/19/80, 09/19/80
(4)sesame: UNCLASSIFIED	2720: silver (z=47.0, a=107.868)	1.050E+01	j. johnson, s. lyon	101 102 103 201 301 303 304 305 306 401	02/09/88, 02/11/88
(5)sescu1: UNCLASSIFIED	22724: silver	9.330E+00	G. Rinker	101 102 201 601 602 603 604	08/04/87, 08/04/87
(6)sescu9: UNCLASSIFIED	22729: silver	1.050E+01	Scott L. Woodside and Arthur E. Greene	201 602	89/07/24, 89/07/24
(7)sescu: UNCLASSIFIED	22721: silver	9.330E+00	g. rinker	101 102 201 601 602 603 604 605	06/21/84, 07/17/84



be sure to check the density/pressure/temperature range to see if it applies to your problem!

Online examples of SESAME tables

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(2)sesame: UNCLASSIFIED	2721: silver (z= 47.000000 a=107.868000)	1.049E+01	Scott D. Crockett	101 102 201 301 303 304 305 306 311 401 411 412	05/10/11, 05/10/11
(3)sesou: UNCLASSIFIED	12720: silver (z=47, a=107.68)	1.049E+01	lasl t-4	101 102 201 502	09/19/80, 09/19/80
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(7)sescu: UNCLASSIFIED	22721: silver	9.330E+00	g. rinker	101 102 201 601 602 603 604 605	06/21/84, 07/17/84

this table goes with the input file we saw above

Online examples of SESAME tables

A given EOS can have multiple tables

UNCLASSIFIED

Table ID	Words/Table	Words Per Table and Number of Densities and Temperatures with Sample Values				
			Number	1 st Value	2 nd Value	Last Value
101	30					
102	20					
201	5					
301	25460	Density	108	0.0000000E+00	1.0490000E-05	2.0980000E+05
		Temperature	78	0.0000000E+00	7.25303125E+01	1.16048500E+09
303	25460	Density	108	0.0000000E+00	1.0490000E-05	2.0980000E+05
		Temperature	78	0.0000000E+00	7.25303125E+01	1.16048500E+09
304	25930	Density	110	1.0490000E-05	2.0980000E-05	2.0980000E+05
		Temperature	78	0.0000000E+00	7.25303125E+01	1.16048500E+09
305	25930	Density	110	1.0490000E-05	2.0980000E-05	2.0980000E+05
		Temperature	78	0.0000000E+00	7.25303125E+01	1.16048500E+09
306	443	Density	110	1.0490000E-05	2.0980000E-05	2.0980000E+05
		Temperature	1	0.0000000E+00	-1.96936613E-10	0.0000000E+00
311	25460	Density	108	0.0000000E+00	1.0490000E-05	2.0980000E+05
		Temperature	78	0.0000000E+00	7.25303125E+01	1.16048500E+09
401	289	Density	36	3.58322359E-12	1.30092430E-11	0.0000000E+00
		Temperature	0	7.25303125E+01	1.45060625E+02	0.0000000E+00
411	543	Density	108	0.0000000E+00	1.0490000E-05	2.0980000E+05
		Temperature	1	0.0000000E+00	0.0000000E+00	0.0000000E+00
412	543	Density	108	0.0000000E+00	1.0490000E-05	2.0980000E+05
		Temperature	1	0.0000000E+00	0.0000000E+00	0.0000000E+00

LA-UR-09-00450, LA-UR-09-00451, LA-UR-08-03679, LA-UR-08-03679, LA-UR-08-03679

Online examples of SESAME tables

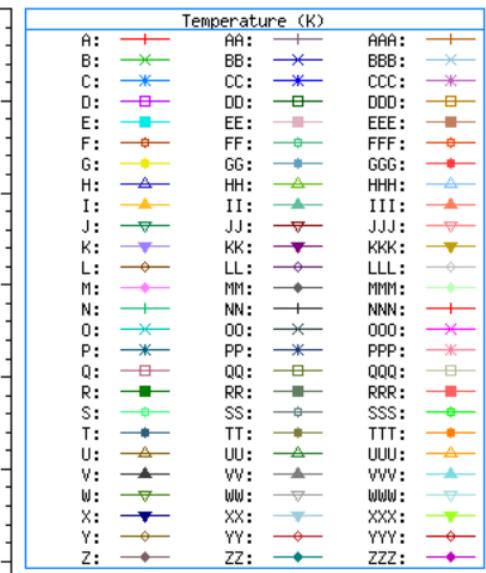
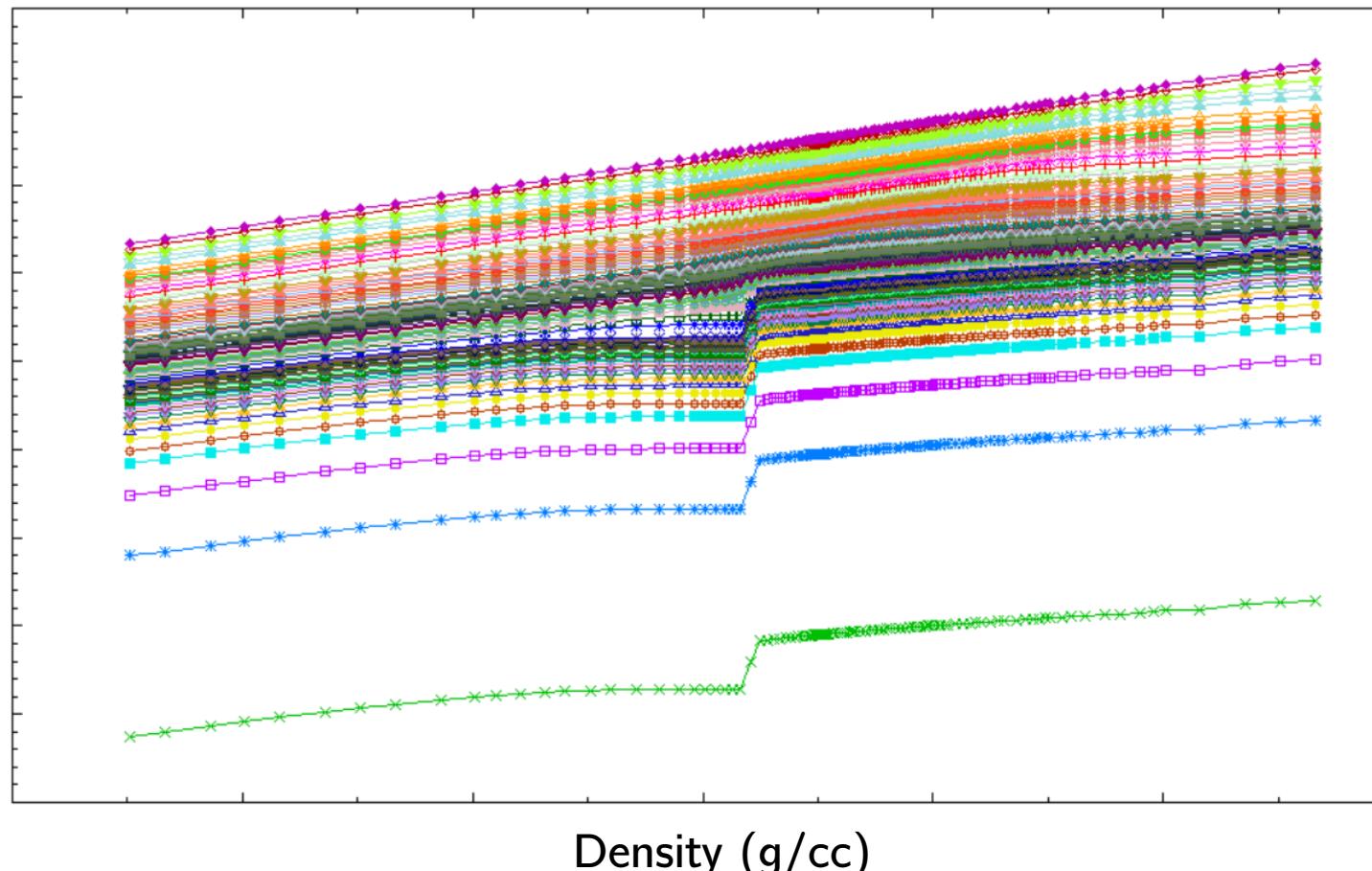
Complete SESAME table for silver (Ag)

UNCLASSIFIED Source Data File:sesame

Sesame Material:2721 Table:304 Material Name: silver (z= 47.000000 a=107.868000)
Pressure (GPa)

UNCLASSIFIED Source Data File:sesame Sesame Material:2721 Table:304 Material Name: silver (z= 47.000000 a=107.868000)

Pressure (GPa)



Density (g/cc)

LA-UR-09-00450, LA-UR-09-00451, LA-UR-08-03679, LA-UR-08-03679, LA-UR-08-03679

Online examples of SESAME tables

Complete SESAME table for silver (Ag)

You can also look at the values throughout the table in the online version

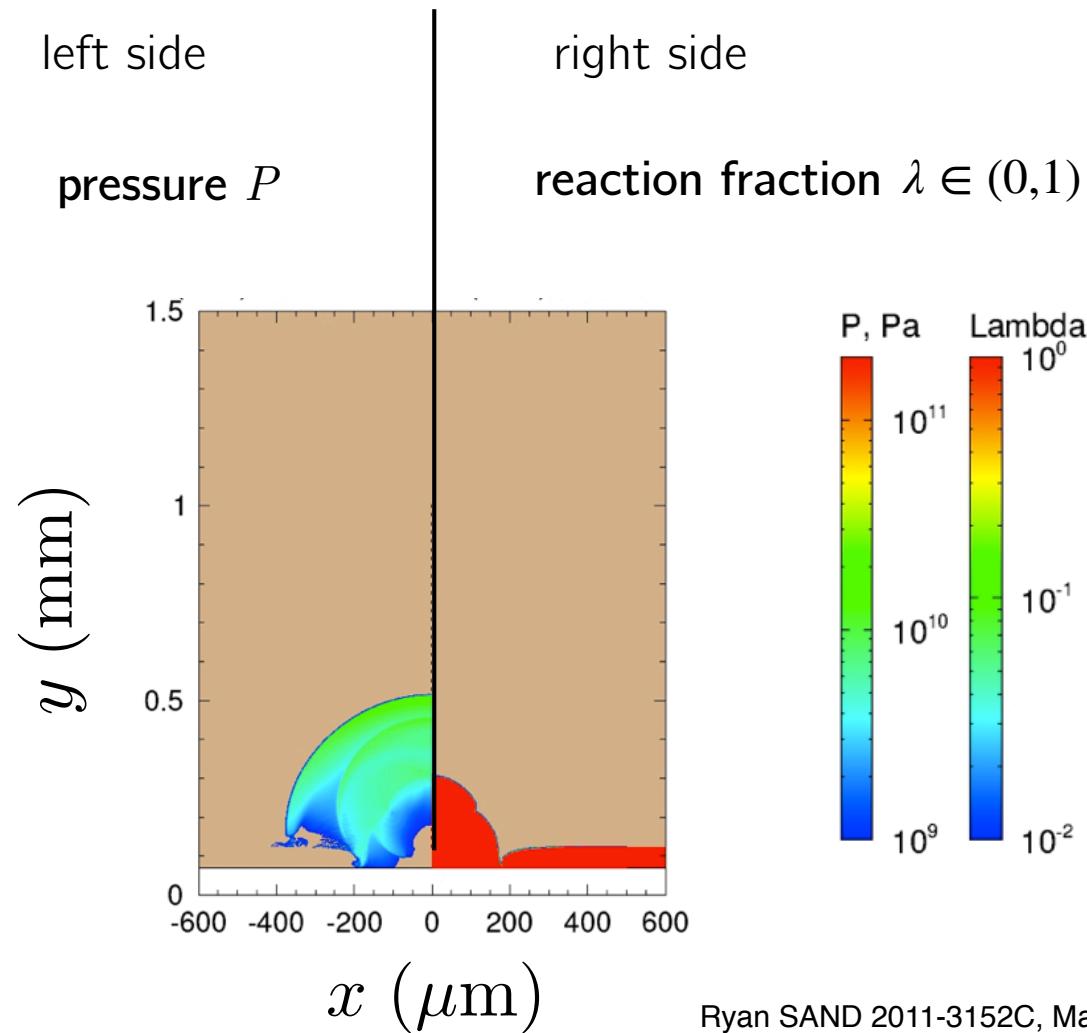
UNCLASSIFIED Source Data File:sesame
Sesame Material:2721 Table:304 Material Name: silver (z= 47.000000 a=107.868000)
Pressure (GPa)

[110] Density (g/cm3)=> =====	1.049000000000e-05	2.098000000000e-05	5.245000000000e-05	1.049000000000e-04	2.098000000000e-04	5.245000000000e-04	1.049
A:0.000000000000000E+00	0.000000000000000E+00						
B:7.25303125000001E+01	5.565567700591279E-27	9.996903269629076E-27	2.133864609440955E-26	3.734064065823262E-26	6.442635370874825E-26	1.291376810405186E-25	2.13474
C:1.450606250000000E+02	9.482388405337518E-17	1.703231813048300E-16	3.63559193233033E-16	6.361946832268033E-16	1.097670071179091E-15	2.200195407308935E-15	3.63708
D:2.175909375000000E+02	2.439985041212962E-13	4.382714531305851E-13	9.355016427985457E-13	1.637040631555280E-12	2.824497836807199E-12	5.661489122885356E-12	9.35885
E:2.981518062000000E+02	1.699849903074505E-11	3.053279731395388E-11	6.517303794807789E-11	1.140467384789754E-10	1.967726151199718E-10	3.944156039583722E-10	6.51997

Example 1: two EOS leading to different results

Detonation of HNS (explosive) at $t = 0$

look at two different hydro simulations with all the same parameters, but two different EOS



Ryan SAND 2011-3152C, Mattsson SAND 2011-8867C

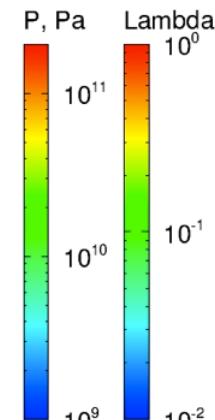
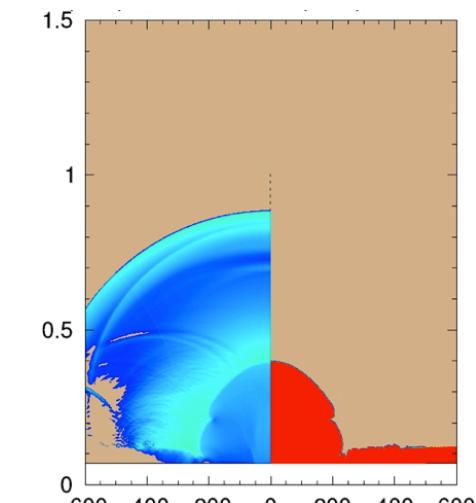
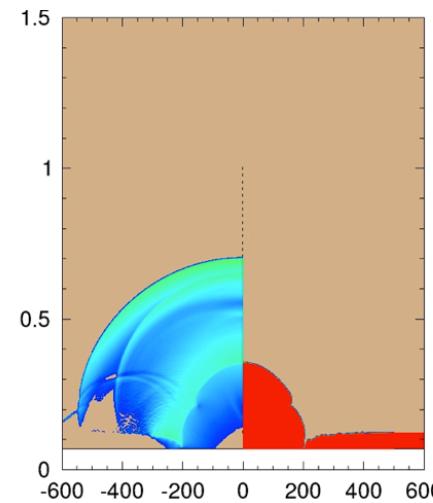
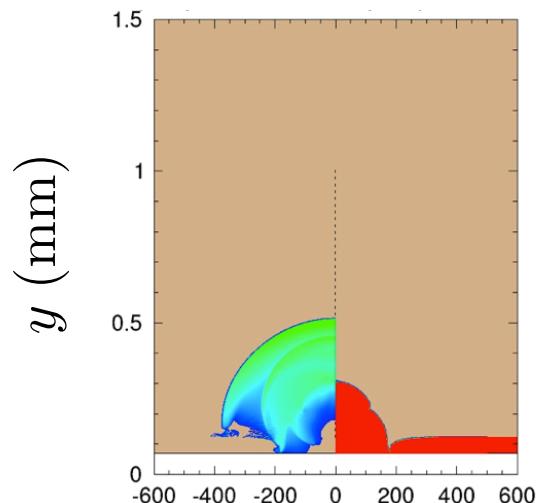
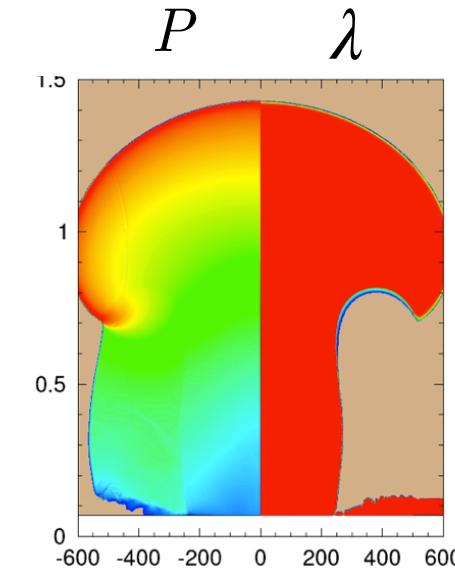
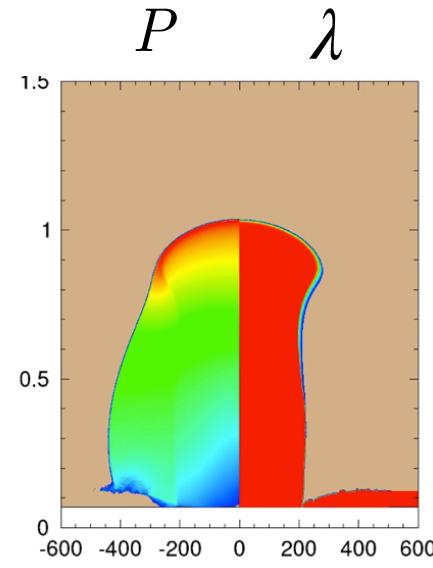
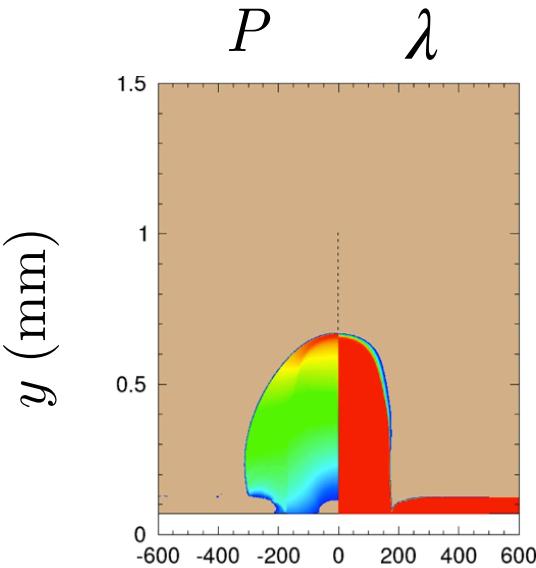
Example 1: two EOS leading to different results

time

$\longrightarrow t_1$

t_2

$\longrightarrow t_3$



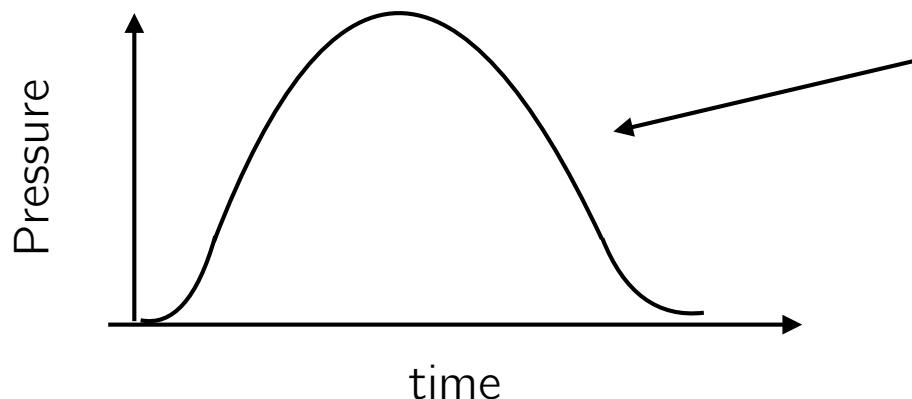
Example 2: kinetics of phase transitions

Tin rod

- hit the rod with a pressure pulse at $x = 0$



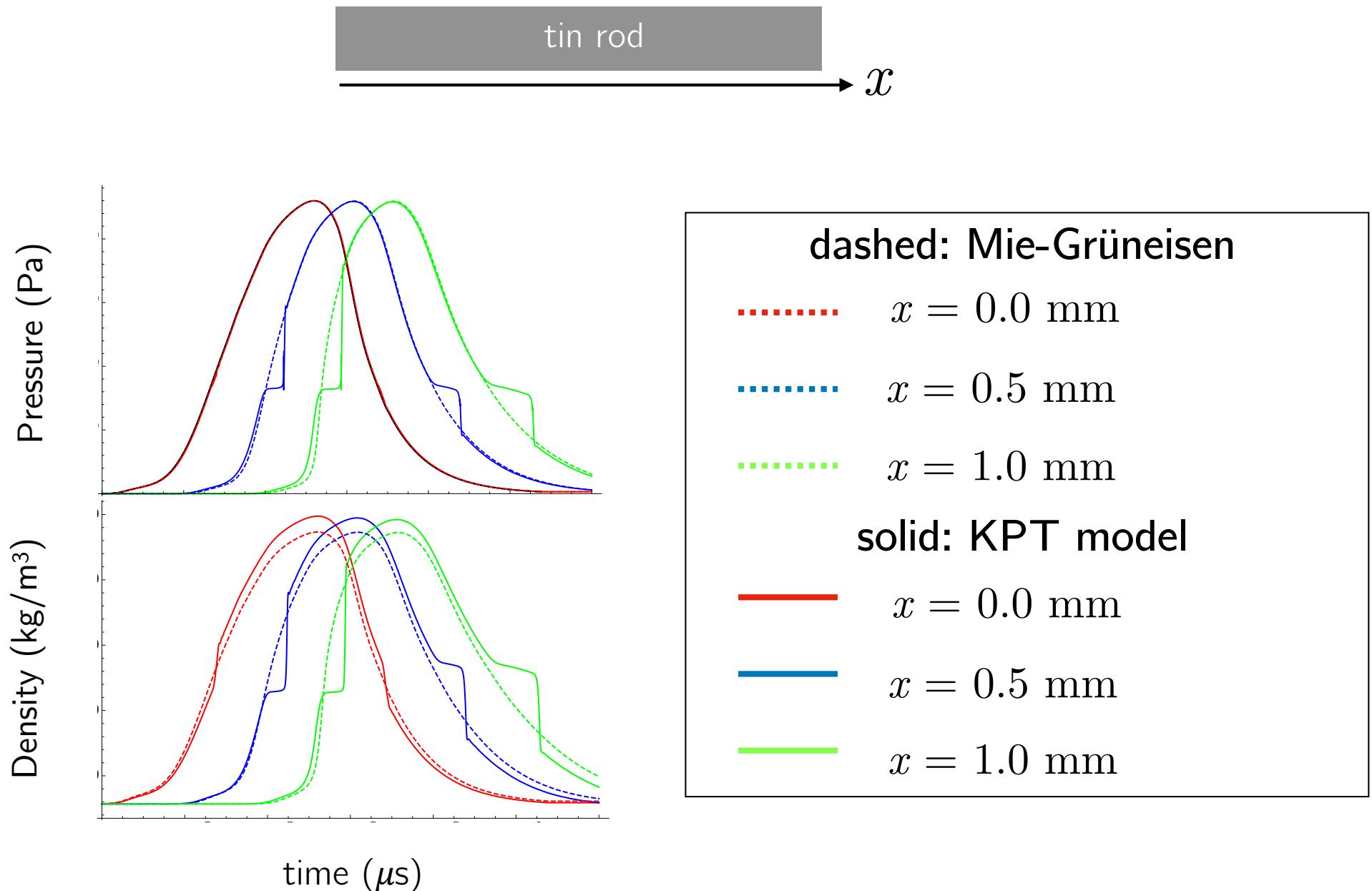
at $x = 0$



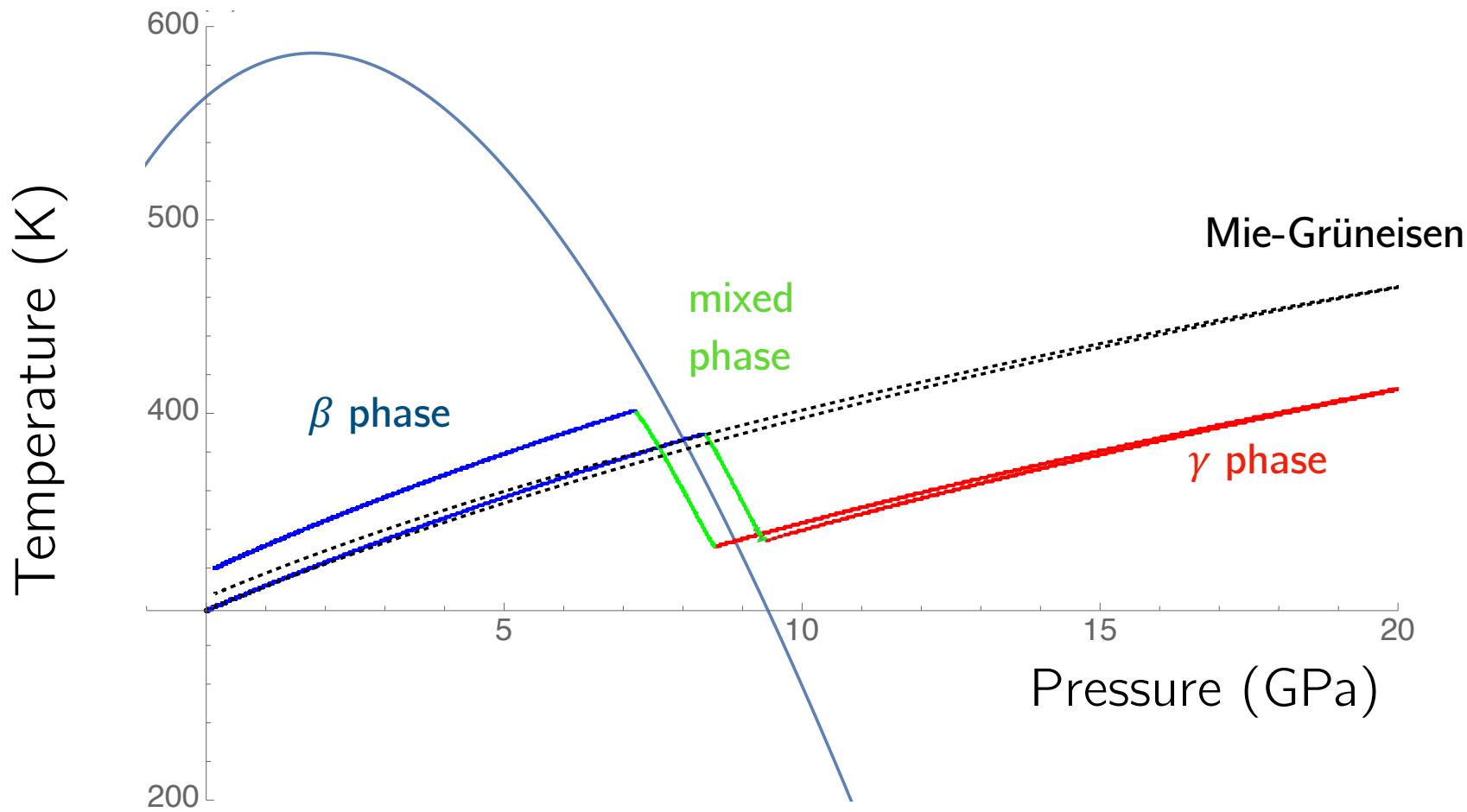
pressure wave at $x=0$ leads
to a traveling pressure wave through
the material

Q: what does the pressure in the material
look like in time?

Example 2: kinetics of phase transitions



Example 2: kinetics of phase transitions



Conclusions

- ▶ Many approximations and models go into an EOS
- ▶ Always look at the EOS table information to figure out if the range of P , T , ρ , etc. is valid for your hydro simulation!
- ▶ Two EOS that both have a valid range can lead to different results in the hydro code
- ▶ EOS development is an active field of research, so be on the lookout for new EOS tables that incorporate new models!